Geochimica et Cosmochimica Acta

JOURNAL OF THE GEOCHEMICAL SOCIETY

xecutive
Editors

ditors

C. W. CORRENS, *Göttingen.* E. INGERSON, *Austin, Texas.* L. R. WAGER, *Oxford.*

L. H. AHRENS, *Capetown.* S. R. NOCKOLDS, *Cambridge.* H. C. UREY, *La Jolla, Calif.*
JOHN VERHOOGEN, *Berkeley, Calif.* A. P. VINOGRADOV, *Moscow.*
W. A. WAHL, *Helsingfors.*

CONTENTS VOLUME 20, NO. 2 OCTOBER 1960

S. R. TAYLOR: Abundance and distribution of alkali elements in australites 85

J. H. REYNOLDS: Rare gases in tektites 101

M. A. VAN DILLA, J. R. ARNOLD and E. C. ANDERSON: Spectrometric measurement of natural and cosmic-ray induced radioactivity in meteorites 115

G. W. REED, K. KIGOSHI and A. TURKEVICH: Determinations of concentrations of heavy elements in meteorites by activation analysis . . 122

ANN DUFRESNE: Selenium and tellurium in meteorites 141

MARY VOGT WOODLAND: Data of rock analyses—VII. Bibliography and index of rock analyses in the periodical and serial literature of the Republic of Ireland and of Northern Ireland 149

Geochemical Notes:

B. J. RUSHTON: Beryllium in Tanganyika granitic rocks 154

A. E. RINGWOOD: Cohenite as a pressure indicator in iron meteorites . 155

L. R. WAGER: The relationship between the fractionation stage of basalt magma and the temperature of the beginning of its crystallization . 158

E 351
425

PERGAMON PRESS OXFORD · LONDON · NEW YORK · PARIS

GEOCHIMICA ET COSMOCHIMICA ACTA

EXECUTIVE EDITORS

PROF. C. W. CORRENS (1959) *Sedimentpetrographisches Institut der Universität, Lotzestr.* 13, *Göttingen, Germany*
PROF. E. INGERSON (1959–1960) *Department of Geology, University of Texas, Austin* 12, *Texas, U.S.A.*
PROF. L. R. WAGER, F.R.S. (1959–1961) *Department of Geology and Mineralogy, The University Museum, Oxford, England*

EDITORS

PROF. L. H. AHRENS (1959–1960) *Department of Chemistry, University of Capetown, Rondebosch, Cape Province, South Africa*
Dr. S. R. NOCKOLDS *Department of Mineralogy and Petrology, The University, Cambridge, England*
PROF. H. C. UREY, For. Mem. R. S. (1959) *University of California, La Jolla, California, U.S.A.*
Dr. JOHN VERHOOGEN (1959–1961) *Department of Geology, University of California, Berkeley, California, U.S.A.*
PROF. A. P. VINOGRADOV (1959–1961) *Vernadsky Institute, Moscow, U.S.S.R.*
PROF. W. A. WAHL (1959–1961) *Observatoriegaten* 8, *Helsingfors, Finland*

EDITORIAL ADVISORY BOARD

EUROPE

T. F. W. BARTH, *Oslo*
L. CAPDECOMME, *Toulouse*
E. J. CONWAY, *Dublin*
P. ESKOLA, *Helsinki*
P. GALLITELLI, *Modena*
A. HADDING, *Lund*
O. HAHN, *Göttingen*
H. W. HARVEY, *Plymouth*
F. HEIDE, *Jena*
A. HOLMES, *Edinburgh*
W. Q. KENNEDY, *Leeds*
PH. H. KUENEN, *Gröningen*
S. LANDERGREN, *Stockholm*
F. MASHATSCHKI, *Vienna*
A. MUIR, *Harpenden*
J. ORCEL, *Paris*
E. RAGUIN, *Paris*
E. REINHARD, *Basle*
TH. G. SAHAMA, *Helsinki*
C. E. TILLEY, *Cambridge*
T. VOGT, *Trondheim*

AMERICAN CONTINENT

A. F. BUDDINGTON, *Princeton*
D. GUIMÃRAES, *Belo Horizonte*
G. E. HUTCHINSON, *New Haven*
B. H. MASON, *New York*
F. WHIPPLE, *Cambridge*
R. WILDT, *New Haven*
H. S. YODER, *Washington*

FAR EAST

T. WATANABE, *Tokyo*

Publishing Offices: Pergamon Press Ltd., Headington Hill Hall, Oxford

Four issues per volume, three volumes per year

Subscription *per annum* (including postage) (A) £21 (U.S.A. $60.00); (B) For individual subscribers who write directly to the publisher certifying that the Journal is for their private use, £7. 7s. (U.S.A. $21.50). Members of the Geochemical Society, or non-members who occasionally publish papers in the Journal, £3. 11s. 6d. (U.S.A. $10.00) *per annum*.

Back numbers, £10 (U.S.A. $28.00) per volume

Single issues, £2. 10s. (U.S.A. $7.00) each

Copyright © 1960 Pergamon Press Ltd.

PERGAMON PRESS LTD.

HEADINGTON HILL HALL, OXFORD 122 EAST 55TH STREET, NEW YORK 22, N.Y.

PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS, BELFAST.

Introducing a most important and authoritative new encyclopedia...

THE INTERNATIONAL ENCYCLOPEDIA OF PHYSICAL CHEMISTRY AND CHEMICAL PHYSICS

Editors-in-Chief:

E. A. GUGGENHEIM, Reading **J. E. MAYER,** California (La Jolla)

F. C. TOMPKINS, Imperial College, London

Chairman of the Editorial Advisory Group:

I. R. MAXWELL, Publisher at Pergamon Press

The International Encyclopedia of Physical Chemistry and Chemical Physics is to be an authoritative and comprehensive presentation of the domain of knowledge which lies between and overlaps chemistry and physics. Each volume—between 50 and 100 volumes are now planned—will be written primarily for the physical chemist and chemical physicist but many volumes will be of value to other scientists: to chemists and physicists generally and also to biochemists and biophysicists.

The Encyclopedia is international in character and will be produced to the highest professional and editorial standards. It is being written in English as this is the language understood, if not spoken, by the greatest number of scientists.

When completed the Encyclopedia will be a compendium and synthesis of physical chemistry and chemical physics as these subjects stand at mid-century. It will be a landmark in scientific publishing and will be used for many years by scientists, university teachers and students.

Nearly 100 volumes will be published (with the assistance of a distinguished board of responsible editors) grouped in the following topics...

1 MATHEMATICAL TECHNIQUES
Editor: **H. JONES**

2 CLASSICAL AND QUANTUM MECHANICS
Editor: **PER-OLOF LÖWDIN**

3 ELECTRONIC STRUCTURE OF ATOMS
Editor: **CLYDE HUTCHISON, Jr.**

4 MOLECULAR BINDING
Editor being appointed

5 MOLECULAR PROPERTIES
(a) Electronic
Editor being appointed
(b) Non-electronic Editor: **N. SHEPPARD**

6 KINETIC THEORY OF GASES
Editor: **E. A. GUGGENHEIM**

7 CLASSICAL THERMODYNAMICS
Editor: **D. H. EVERETT**

8 STATISTICAL MECHANICS
Editor: **J. E. MAYER**

9 TRANSPORT PHENOMENA
Editor: **J. E. MAYER**

10 THE FLUID STATE
Editor: **J. S. ROWLINSON**

11 THE IDEAL CRYSTALLINE STATE
Editor: **M. BLACKMAN**

12 IMPERFECTIONS IN SOLIDS
Editor: **A. B. LIDIARD**

13 MIXTURES, SOLUTIONS, CHEMICAL AND PHASE EQUILIBRIA
Editor: **M. L. McGLASHAN**

14 PROPERTIES OF INTERFACES
Editor: **D. H. EVERETT**

15 EQUILIBRIUM PROPERTIES OF ELECTROLYTE SOLUTIONS
Editor: **R. A. ROBINSON**

16 TRANSPORT PROPERTIES OF ELECTROLYTES
Editor: **R. H. STOKES**

17 MACROMOLECULES
Editor: **C. E. H. BAWN**

18 DIELECTRIC AND MAGNETIC PROPERTIES
Editor: **WILLARD STOUT**

19 GAS KINETICS
Editor: **A. F. TROTMAN-DICKENSON**

20 SOLUTION KINETICS
Editor: **R. M. NOYES**

21 SOLID AND SURFACE KINETICS
Editor: **F. C. TOMPKINS**

22 RADIATION CHEMISTRY
Editor: **ROBERT LIVINGSTON**

Just published in Topic 6

Volume 1

ELEMENTS OF THE KINETIC THEORY OF GASES

by **E. A. Guggenheim,** M.A., Sc.D., F.R.S.

This volume describes in an elementary way the most important features of the kinetic theory of gases, and as such will prove most useful to physical chemists and chemical physicists who would not normally have a standard of mathematics necessary for the more advanced treatments.
The author is known for his researches and several books on thermodynamics and related matters, but this is his first book on non-equilibrium properties.

17s. 6d. ($3.00)

Write now for fully descriptive leaflet of this outstanding encyclopedia

PERGAMON PRESS

OXFORD LONDON NEW YORK

Headington Hill Hall, Oxford 4 & 5 Fitzroy Square, London W.1
122 East 55th Street, New York 22, N.Y.

A selection of titles from Pergamon Press

Boundary Layer and Flow Control - Principles and Applications

Two volumes

Edited by **G. V. LACHMANN**

These books contain contributions by 38 international authorities and encompass the entire field of boundary layer control. Most of these contributions contain information or disclose methods either novel or additive to previously published work. The historical chapter is the most comprehensive report that has ever been published.

£10 10s. net ($35.00) per set

Inertial Guidance

by **C. S. DRAPER, W. WRIGLEY** *and* **J. HOVORKA**

This treatise in the International Series on Aeronautical Sciences and Space Flight describes the physical principles and engineering methods underlying the navigation and control of vehicles solely by means of signals from sensors that depend only on the inertial properties of matter for their operation. There is a completely up-to-date bibliography.

42s. net ($6.50)

Avionics Research

Satellites and Problems of Long Range Detection and Tracking

Edited by **E. V. D. GLAZIER, E. RECHTIN** *and* **J. VOGE**

This volume contains the proceedings of the symposium held in Copenhagen by the Avionics Panel of the Advisory Group for Aeronautical Research and Development, N.A.T.O. The papers in this volume show how the study of the physical environment is important for all operations in the high atmosphere and space, indicating areas for basic physical research to be carried out co-operatively among N.A.T.O. countries. Illustrated.

63s. net ($10.00)

Advanced Propulsion Systems

Edited by **M. ALPERIN** *and* **G. P. SUTTON**

In this book many new and imaginative concepts of physical propulsion, power sources, propellants and human hazards are explored in the light of present knowledge and scientifically predicated conjecture.

42s. net ($6.00)

Rarefied Gas Dynamics

PROCEEDINGS OF THE FIRST INTERNATIONAL SYMPOSIUM HELD AT NICE

Edited by **F. M. DEVIENNE**

Papers on design and theory, as well as experimental aspects of the subject, are included. Internationally recognized experts from many countries took part.

£6 net ($17.50)

Plasma Dynamics

A SYMPOSIUM SPONSORED BY THE U.S. AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

General Editor: **F. H. CLAUSER**

Participants in the symposium came from the fields of astrophysics, fluid mechanics, thermonuclear physics, gaseous discharges, electron beam dynamics and statistical mechanics. This volume also contains references and an extensive bibliography. PLASMA DYNAMICS undoubtedly gives as broad and informative a picture of this field as has yet been presented.

84s. net

Unsteady Motion of Continuous Media

by **K. P. STANYUKOVICH**

No previous knowledge of gas dynamics is required to appreciate this volume which contains, for the first time, a complete account of contributions to this field by Russian scientists

£5 net ($15.00)

Fully descriptive leaflets on request

PERGAMON PRESS OXFORD LONDON NEW YORK

Headington Hill Hall, Oxford 4 & 5 *Fitzroy Square, London W.*1.

122 *East 55th Street, New York* 22, *N.Y.*

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 85 to 100. Pergamon Press Ltd. Printed in Northern Ireland

Abundance and distribution of alkali elements in australites

S. R. Taylor
Department of Geochemistry, University of Cape Town

(*Received* 10 *May* 1960)

Abstract—Sodium and potassium have been determined by flame photometric methods and lithium, rubidium and caesium by emission spectrographic techniques in fourteen australites from Western Australia, South Australia and the Northern Territory. Arithmetic means of the analytical data are: Li, 42 p.p.m; Na, 0·95 per cent; K, 1·89 per cent; Rb, 84 p.p.m; Cs, 2·7 p.p.m. These figures are of the same order of magnitude as terrestrial abundances, and match the abundances in sedimentary rocks somewhat better than those for igneous rocks. The averages for sodium and potassium are virtually identical to those found by Pinson and Schnetzler (1959) for eleven philippinites and indochinites. The dispersion in concentration of the alkali elements is much smaller than in specific terrestrial rock types such as granites, but is distinctly greater than the small dispersion found in chondrites. It is a significant variation, being greater than the limits of analytical precision for the individual elements.

All the elements show a close association with one another. Co-efficients of correlation (r) range from +0·730 for the pair Li–Rb to +0·962 for the pair Na–K, and the degree of correlation is statistically "highly significant." It is concluded that such a coherence arises from a physical process such as mixing, rather than by chemical means.

A regional variation in composition, with higher concentrations of alkali elements towards the west of Australia, is observed.

Introduction

The sodium and potassium content of tektites has been frequently determined, but only a few workers (Goldschmidt *et al.*, 1933; Pinson *et al.*, 1953; Pinson *et al.*, 1958; and Cohen, 1959) have made estimates of the abundance of the rare alkali elements, lithium, rubidium and caesium in these enigmatic glassy bodies. The figures for lithium and rubidium given by Cohen (1959) are very much in excess of the amounts in common terrestrial materials, and of those reported by the other workers. These figures, if correct, might preclude a terrestrial origin for tektites.

Pinson and Schnetzler (1959) have reported that eleven philippinites and indochinites have rather uniform concentrations of Na (1·0 $\pm$ 0·1 per cent); K (1·9 $\pm$ 0·1 per cent); Fe, Mn and Ti. Uniformity of composition for groups of tektites, if established, would have far-reaching implications.

It seemed, therefore, desirable to make careful determinations of the alkali elements in one group of tektites. The australites are very suitable for such a purpose, being abundant, geologically youthful, well preserved and, with the indochinites, the best described of the several groups (Baker, 1959). We are rather well informed about the geochemistry of the alkali elements, and significant comparisons can be made between the terrestrial and tektite abundances.

Analytical Methods

These are given in detail to enable full comparison to be made with other published data.

Sample preparation. The tektites were sawn in two and one portion was washed and crushed in a surface-hardened "Pitho" steel mortar to pass 120-mesh nylon cloth held in a plastic sieve holder. A hand magnet was used to remove iron contamination from the sample after drying at 140°C. The magnet was not brought into physical contact with the sample.

Sodium and potassium. These elements were determined by a flame photometric procedure,

using an Eel model A flame photometer (Evans Electroselenium Co., Harlow, Essex, England). All glassware was Pyrex brand. Filter funnels and storage bottles were polythene. B.D.H. "AnalaR" chemicals were employed exclusively. The ammonium carbonate solution was prepared by dissolving 10 g of AnalaR $(NH_4)_2CO_3$ in 50 ml H_2O and 50 ml AnalaR ammonia solution (about 25% NH_3) and was kept in a polythene bottle.

About 150 mg of the powdered sample was accurately weighed into a platinum dish, 2 ml 50% H_2SO_4 and 4 ml HF were added, and digested on a hot plate at about 125°C. After evaporation to dryness, one drop of 50% H_2SO_4 was added and about 50 ml H_2O. After all the soluble material had dissolved, the contents of the dish were transferred quantitatively through a

Table 1. Values of Na and K in standards

		Na (%)	K (%)
G–1*	Granite	2·41	4·50
W–1*	Diabase	1·48	0·53
USBS.89†	Lead–barium glass	4·23	6·97
USBS.99†	Soda feldspar	7·66	0·34

* Fairbairn (1953).
† U.S. Bureau of Standards standard samples.

polythene funnel into a 250 ml standard Pyrex flask. A slight amount of insoluble material was observed in sample no. 415, but all the other australite samples dissolved completely. 2·5 ml of the ammonium carbonate solution was added and after standing for 10 min, the solution was filtered through a Whatman no. 41 paper into a polythene bottle.

The flame photometer was operated on laboratory gas, and air at 10 lb in^2. The dilutions employed for the samples gave galvanometer deflections in the range from 64 to 75 for potassium and from 57 to 75 for sodium. Air pressure, the zero setting and calibration of the instrument with standards giving readings close to those of the unknowns were checked before and after each sample reading. Instrumental drift was in fact small. For each element, determinations were made in 1 day, and the working curve was established at the same time.

The standards listed in Table 1 were used to establish the working curves. Because of possible matrix effects, silicate standards were used in preference to those prepared by dissolving simple salts. Working curves, that is, graphs relating concentration of elements in standards to an instrumental measurement of emitted intensity of radiation from the element, are shown in Fig. 1. The symbols G–1/2; G–1/4, etc., refer to successive dilutions of the standard G–1 by factors of 2 and 4.

Lithium and rubidium. These elements were determined by optical spectrography, using the variable internal standard procedure for the alkali elements (Ahrens and Taylor, 1960, Section 13–3).

Operating conditions were as follows: Spectrograph: Hilger large quartz and glass (E.478). Optical arrangement: glass prism; Hilger F.958 lens focussed on slit. Seven-step sector (2 : 1 ratio). Slit width: 10 μ. Wavelength range: 4600–9600 Å. Kodak IN plate. Current: 3 A d.c. (short-circuit setting); anode excitation. Lower electrode (anode): National Carbon Co. Special graphite $\frac{3}{16}$ in. rod (cat. no. L.3863); internal diameter of crater: $\frac{3}{32}$ in. (2·4 mm); depth: 2·5 mm; wall thickness: 0·5 mm. Two exposures were superimposed for each sample. Upper electrode (cathode): National Carbon Co. special carbon (cat. no. L.3806) $\frac{1}{8}$ in. rod.

The unmixed sample powders were arced until the end of the alkali metal distillation period (Ahrens and Taylor, 1960, Section 13–3). Plates were developed for 4 min in Kodak D-19b developer at 20°C. Lines were read with a Hilger non-recording microphotometer set at a clear plate galvanometer deflection of 50. Sodium was used as the internal standard, and the following lines were read: Na 5688, Li 6103, Rb 7800 and Rb 7947.

Li 6103·642 is liable to interference from Ca 6102·721 (intensity listing of 80 in the M.I.T. tables, Harrison, 1939) in calcium-rich specimens (Ahrens, 1954b, p. 58) and this was observed

in W–1. A check is provided by Ca 6122·218, which has an intensity listing of 100 in the M.I.T. tables (HARRISON, 1939). Some $CaCO_3$ containing a very small amount of lithium (Li 6707 was faintly visible) was arced and the ratio I Ca 6103: I Ca 6122 was determined as 0·28. In this case, using a step sector with a 2 : 1 intensity ratio, interference will result from Ca 6103 if Ca 6122 is clearly visible on two steps. Ca 6122 was occasionally faintly visible on the second step of the spectra used to determine lithium. It was clearly visible on the third step of the spectra used to determine caesium (for which larger electrodes were used), and thus these plates were not

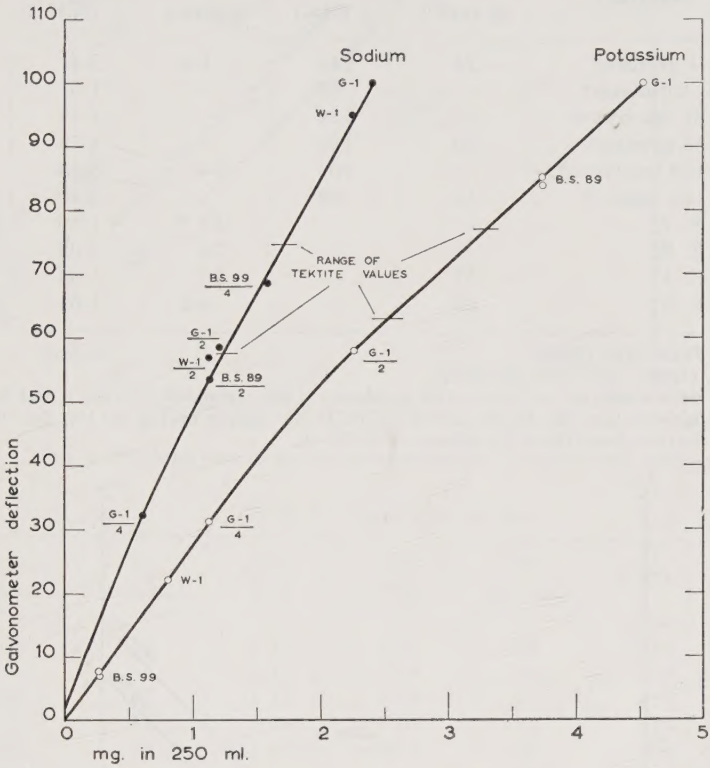


Fig. 1. Working curves for the determination of sodium and potassium.

used to determine Li. It may thus safely be concluded that no interference of Li 6103 by Ca 6103 in fact occurred. The use of Li 8126 (1000) which is a weaker line was not attempted because it was subject to halation by the sodium doublet, Na 8183, 8194, and also because of general background due to red CN emission. Li 6707, a frequently used line for the determination of the element, is too intense to be satisfactory, particularly since it is liable to self-absorption. Plate calibration was by the self calibration method (AHRENS and TAYLOR, 1960, Section 11–5).

Caesium. The same general method as described above was used. Larger anodes were used (internal diameter of crater: $\frac{1}{8}$ in. (3·2 mm); depth: 5 mm; wall thickness: 0·5 mm; National Carbon Co., special graphite, cat. no. L3863). Cs 8521 was read, and Na 5688 was the internal standard. Background corrections were made and intensities for the background were obtained in the same way as the line intensities. The background for the Cs line was read at about λ 8530. Fe 8514 was occasionally present but was well resolved from Cs 8521. No interference was observed from Ti 8518 (100 intensity rating in the M.I.T. tables). Other nearby Ti lines of much greater intensity (e.g. Ti 8435; 350 rating in the M.I.T. tables) were not observed.

Standards for Li, Rb *and* Cs. Natural silicate standards were used exclusively because of the well known matrix problems in emission spectrochemical analysis. The values used are given in Table 2. Working curves based on these standards are shown in Fig. 2 (Rb) and 3 (Li and Cs).

Analytical results are given in Table 3. The analytical precision (expressed as relative deviation, C) for each method is given in Table 4, and, in the same table, is shown for comparison, the scatter of the experimental results, calculated as a relative deviation. The precision of the analytical methods was calculated from replicate determinations on individual samples.

Table 2. Standards used for the determination of Li, Rb and Cs.

Standard	Li (p.p.m.)	Rb (p.p.m.)	Cs (p.p.m.)	Na (%)
G–1 granite*	24	240	1·5	2·4
W–1 diabase*	—	22	—	1·5
T.81 trachyte†	—	132	—	4·11
T.85 syenite†	30	105	—	4·75
T.123 trachyte†	—	206	34	5·15
T.124 basalt†	11	39	—	2·80
L.F. 2‡	—	—	144	1·90
L.F. 3‡	—	—	72	2·02
L.F. 4‡	57	—	15	1·54
L.F. 5‡	32	—	8·2	1·55

* Ahrens and Fleischer (1960).
† Taylor *et al.* (1956), and Taylor (1954).
‡ L.F. 2 and 3 were made by mixing A-106 lepidolite (1440 p.p.m. Cs; Cabell and Smales, 1957; 0·31% Na) with K-feldspar (no. 52: Heier and Taylor, 1959; 0·2 p.p.m. Li; 2·11% Na; 1·1 p.p.m. Cs). L.F. 4 and 5 were derived from these by dilution with W–1.

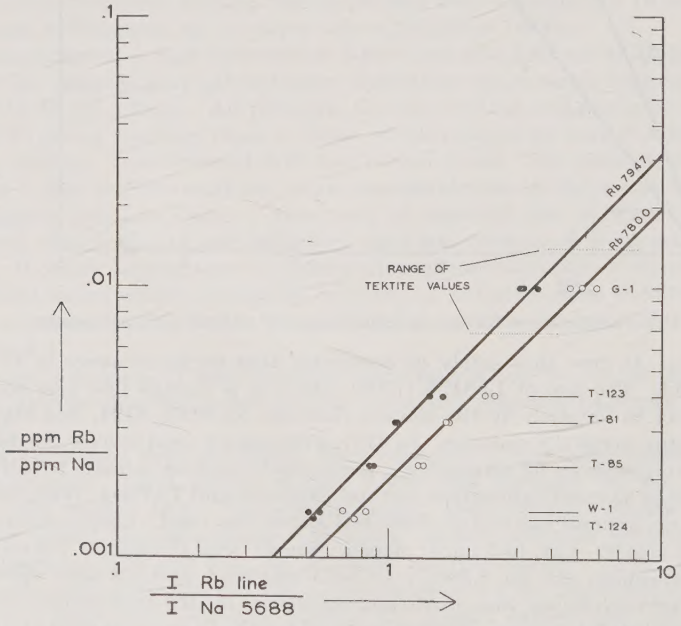


Fig. 2. Working curves for the determination of rubidium.

Geochemical Discussion

Lithium

Few determinations of Li in tektites have been made. Goldschmidt *et al.* (1933) report 14 p.p.m. in a moldavite. Cohen (1959) reports 650 p.p.m. Li in

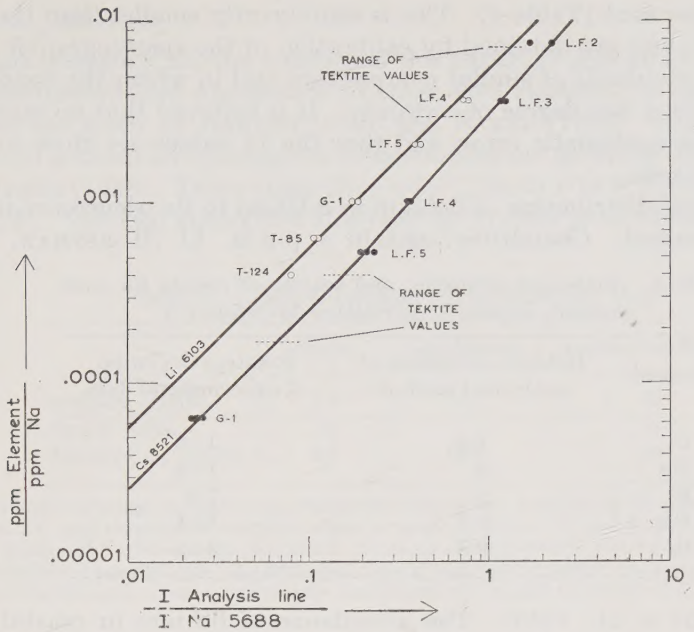


Fig. 3. Working curves for the determination of lithium and caesium.

Table 3. Analytical results

Sample number	Li (p.p.m.)	Na (%)	K (%)	Rb (p.p.m.)	K/Rb	Cs (p.p.m.)
1176	52	1·12	2·12	99	214	4·2
541	48	1·12	2·11	94	224	3·7
463	47	1·13	2·04	97	210	3·8
532	41	1·03	2·03	93	218	3·5
379	46	1·08	2·03	94	216	3·8
229	40	0·86	1·86	81	230	2·0
794	39	0·90	1·85	80	231	2·7
415	46	0·94	1·84	86	214	2·9
230	38	0·85	1·83	81	226	1·9
1026	37	0·89	1·81	82	221	2·9
295	42	0·83	1·76	65	271	1·4
233	39	0·85	1·74	74	235	1·9
355	38	0·83	1·73	73	237	1·7
475	40	0·85	1·73	77	225	2·0
Average ($\bar{x}$)	42	0·95	1·89	84	227	2·7

two moldavites, and an australite, 100 p.p.m. in a bediasite, and 65 p.p.m. Li in a tektite from Georgia, U.S.A. The Li values given here range from 37 to 52 p.p.m., and average 42 p.p.m. The spread expressed as a relative deviation (C) is $\pm 11{\cdot}0$ per cent. The question arises whether such a small spread of results is a real effect, or merely represents analytical error. The relative deviation of the analytical

method is ±7·6 per cent (Table 4). This is significantly smaller than the range of results. The Li values are obtained by calibration of the spectrographic intensity readings against standards of similar composition and in which the concentration of Li is known with a fair degree of certainty. It is believed that no matrix effect is present to cause systematic error, and that the Li values are close to the true amounts of Li present.

The geochemical distribution of lithium in relation to its occurrence in tektites will now be discussed. Chondrites contain 4 p.p.m. Li (Horstman, 1956) or

Table 4. Analytical precision, and scatter of results for each element, expressed as relative deviation (C)

Element	Relative deviation of analytical method	Relative deviation of experimental data
Li	7·6	11·0
Na	3	12·6
K	3	7·6
Rb	8·3	12·1
Cs	9·9	34·6

3·5 p.p.m. (Pinson *et al.*, 1953). The abundance of lithium in crustal rocks is estimated to be 32 p.p.m. by Ahrens and Taylor (1960, Table 8–2); this figure is based on abundance figures in igneous rocks. Horstman (1956) gives a figure of 29 p.p.m. Li in igneous rocks and 53 p.p.m. for sedimentary rocks. The abundance figures given by Strock (1936) were 65 p.p.m. for igneous rocks and 52 p.p.m. for sedimentary rocks. Strock's average for igneous rocks is thought to be too high, and to have been too heavily weighted by some Li-rich German granites. Horstman gives 40 p.p.m. as the average Li content of granites. Very high values are occasionally reported in these rocks. Bowler (1959) for example, reports values of several hundred p.p.m. Li in the granites and associated aureoles of Devon and Cornwall. On the regional scale, these are minor fluctuations, but complicate the calculation of averages. If only truly intrusive, late stage highly fractionated granites are considered (e.g. the granites of SW England), then the Li average for all granites will be high. If all "granites" are considered, a much lower average will result. One of the problems in arriving at these averages for geological material, using data obtained from instrumental methods of analysis, is to know how accurate are the determinations. We can derive some information about this from the lithium determinations on the standard granite, G–1. This is a fairly typical granite. Ten analysts using three different methods (spectrochemical, flame photometric and isotope dilution) have reported values from 19 to 30 p.p.m. Li. The average is 24 p.p.m., which is of the same order of magnitude as the crustal abundance. Igneous rocks more basic than granites have not been reported to contain more than from 25 to 30 p.p.m., and commonly rather less. The tektite average of 42 p.p.m. is thus close to the average for granites. For sediments (Table 5) there is firm agreement that the Li value in shales is higher than for igneous rocks. A 1 : 1 mixture of shale and sandstone has 37 p.p.m. or 39 p.p.m. depending on whether the data of Strock or Horstman are used.

Sodium and potassium

It is not necessary, for the purpose of this paper, to give an extended discussion of the distribution and abundance of these two elements in australites. Useful summaries are given by Barnes (1940) and Baker (1959). Nine previous determinations of sodium and potassium in australites are given by Barnes (1940) and two by Baker (1956). These range from 0·68% Na to 1·14% Na and from 1·04% K to 2·13% K. The two australites analysed by Pinson *et al.* (1958) both contained 2·1% K.

Table 5. Lithium averages for sedimentary rocks

	Shale	Sandstone	Average sediment
Strock (1936)	57	17	52
Shaw (1954)	55	—	—
Horstman (1956)	66	12*	53

* Horstman's average included one glauconitic sandstone, containing 25 p.p.m. Li, 100 p.p.m. Rb and 9 p.p.m. Cs, and three other samples which average 12 p.p.m. Li and 50 p.p.m. Rb. It is doubtful whether a meaningful average for the alkali elements in sandstones can be arrived at without very precise definitions of sample type. An orthoquartzite should not by definition, contain the alkali elements whereas greywackes and arkoses, feldspathic sandstones etc. might approach the alkali element content of shales.

The arithmetic mean of the sodium determinations reported in this paper is 0·95% Na and the range is from 0·83% to 1·13% Na. The spread of the results, expressed as a relative deviation is ±12·6 per cent. The analytical precision, expressed as a relative deviation is 3 per cent (see Table 4). The arithmetic mean of the potassium determinations given in this work, is 1·89% K and the range is from 1·73% to 2·12% K. This spread, expressed as a relative deviation is ±7·6 per cent, compared with an analytical precision of ±3 per cent (see Table 4). The degree of correlation between the sodium and potassium figures given here is very high ($r = +0{\cdot}962$) and the association between the elements is very close (Fig. 4).

For eleven indochinites and philippinites, Pinson and Schnetzler (1959) report an average of 1·0% Na with a standard deviation of ±0·1 per cent (relative deviation of 10 per cent) and an average of 1·9% K with a standard deviation of ±0·1 per cent (relative deviation of 5·3 per cent). It is of much interest to note the similarity of these results to those given in this paper.

Rubidium

The previous determinations of rubidium in tektites are given in Table 6. Where potassium determinations are available for the same samples, these are given, together with the values for the K/Rb ratios. The determinations by Pinson and co-workers are in general agreement with the results reported in this paper. The australites analysed here have an arithmetic average of 84 p.p.m. Rb and range from 65 p.p.m. to 99 p.p.m.

Of particular interest in our case is the coherence between K and Rb shown in Fig. 4d. Rb increases sympathetically with K (the correlation coefficient is +0·919). The K/Rb ratio varies from 210 to 271 and averages 227. This ratio is thus the

same as for terrestrial material in general. This has been considered by Taylor and Ahrens (1959) as evidence that tektites originated within the solar system. Now if the tektites had a uniform composition, and if the observed variation were due to the imprecision of the analytical techniques employed, we should expect only an accidental correlation between the two elements in the individual samples. Here we have, for all samples, a strong positive correlation between two elements determined by independent methods. Further, this correlation is in accord with

Table 6. Previously published values for potassium, rubidium and K/Rb ratios in tektites

	K (%)	Rb (p.p.m.)	K/Rb
Indochinite*	1·74	76†	229
Indochinite*	1·74	72†	242
Philippinite*	1·83	72†	254
Australite‡	2·1	111	189
Australite‡	2·1	110	190
Indochinite‡	2·2	126	175
Indochinite‡	2·1	110	191
Indochinite‡	—	110	—
Philippinite‡	2·4	141	170
Philippinite‡	—	108	—
Moldavite‡	2·7	130	208
Moldavite§	—	900	—
Moldavite§	—	1000	—
Georgia tektite§	—	600	—
Bediasite§	—	500	—
Australite§	—	800	—

* Pinson *et al.*, 1952.

† Rb results reduced by a factor of 0·4 to conform to systematic shift in values of standards employed (Ahrens, personal communication; see Taylor *et al.*, 1956).

‡ Pinson *et al.*, 1958.

§ Cohen, 1959.

the observed geochemical behaviour of both elements. This evidence seems to establish beyond question that the fourteen tektites analysed here differ slightly, but significantly, in composition. Additional evidence is provided from statistical treatment of the data. The spread of results, expressed as a relative deviation, is 7·6 per cent for K and 12·1 per cent for Rb. The analytical precision, also expressed as relative deviation, is 3 per cent for K and 7·2 per cent for Rb (Table 4). The "scatter" of analytical results is thus much greater than the precision of individual results. Ahrens (1957) and Taylor (1960) have discussed the effects of systematic error in some Rb determinations. Most Rb figures which were determined by emission spectrochemical methods prior to the use of the inter-laboratory standards G–1 and W–1 are higher than more recent determinations and must be considered unreliable. Those which have been determined using these standards with the values recommended by Ahrens (1954b) must be reduced by a factor of 0·4 (Taylor *et al.*, 1956; Taylor, 1960).

The geochemistry of Rb is well known, and the analytical data is more reliable than for Li. The coherence between K and Rb has been frequently demonstrated.

The ratio between K and Rb has been well established at 220–230, and variations outside the normal spread of ratios are the result of special geological conditions (Taylor *et al.*, 1956; Herzog and Pinson, 1956; Taylor and Heier, 1958a, b; Heier and Taylor, 1959; Taylor and Ahrens, 1959). The average of the K figures for tektites reported by Barnes (1940) is 1·91% K (2·3% K_2O) and the highest K figure is 2·99% (3·60% K_2O in a moldavite). Assuming the tektites possess "normal" K/Rb ratios of about 220, as is the case for all published K and

Table 7. Rubidium averages for igneous rocks from Horstman (1956) (column 1); potassium averages (column 2) from Barth (1952, Table 33, p. 69) and Rb values (column 3) calculated from these based on a K/Rb ratio of 220

	(1) Rb (p.p.m.)	(2) K (%)	(3) Rb (p.p.m.)
Granite	170	3·41	155
Syenite*	110	3·73	170
Diorite	110	1·76	80
Gabbro	30	0·74	34

* Rb depletion in syenites has been discussed by Taylor and Heier (1958b).

Rb determinations (Cohen did not report K), we have an upper limit of about 150–200 p.p.m. Rb in tektites. Values of Rb greater than this represent enrichment of Rb relative to K, which requires a special environment and rather extreme conditions of fractionation such as occur in pegmatites (see Taylor *et al.*, 1956; Heier and Taylor, 1959; Taylor and Ahrens, 1959). The high Rb values (500–1000 p.p.m.) of Cohen thus require to be substantiated in view of the interesting problems which they raise.

The problem of comparison of the rubidium values with common terrestrial materials is simplified by the constancy of the K/Rb ratio in both tektites and crustal rocks, meteorites, etc. Horstman gives an average for igneous rocks of 120 p.p.m. Rb, close to the crustal average of 115 p.p.m. (Ahrens and Taylor, 1960). His figures are thought to be reliable and are given in Table 7. In column 2 are given K figures for common igneous rocks from Barth (1952) and Rb figures, derived from these on the basis of a K/Rb ratio of 220, are given in column 3. We see from this table that the intermediate igneous rocks have Rb values similar to the australites, in contrast to Li.

Horstman quotes a figure of 140 p.p.m. Rb for shale, 50 p.p.m. for sandstone† and 110 p.p.m. for average sediment. Canney (1952) gives 280 p.p.m. as the average for sediments. This figure has to be reduced by a factor of 0·4 because of the systematic shift in the Rb values for G–1 and W–1 (Ahrens, personal communication; see Taylor *et al.*, 1956; Taylor, 1960) and so becomes 112 p.p.m., in agreement with Horstman. The tektite average of 84 p.p.m. is not inconsistent

† See footnote to Table 5.

with the Rb content of feldspathic sandstone. Using Horstman's data, a 1:1 mixture of shale and sandstone contains 95 p.p.m. Rb. The Franconia feldspathic sandstone analysed by Horstman has 80 p.p.m. Rb, but only 7 p.p.m. Li, indicating little mica.

Caesium

No previous quantitative caesium determinations in tektites are known to the writer. The average caesium content of the australites analysed here is 2·7 p.p.m. and the range is from 1·7 to 4·2 p.p.m. Expressed as a relative deviation, the spread is 34·6 per cent. The precision of the analytical technique, expressed in the same terms (C) is 9·9 per cent. This is the greatest deviation of the elements determined here. Probably it results partly from the necessity for background corrections, a fertile source of error in spectrochemical methods. The spread of the results from the different specimens is well outside the precision limits for their determination, and indicates that there are real differences in composition.

Chondrites contain 0·12 p.p.m. Cs (Ahrens *et al.*, 1960). The amount of reliable geochemical data for caesium is not large. Its concentration is frequently close to its spectrochemical detection limit, where analytical precision is low, and it has most frequently been determined in those potassium minerals in which it is enriched in pegmatites and granites. Horstman reports 1 p.p.m. Cs in granites and less than 1 p.p.m. in other igneous rocks. The figure for granites is lower than usually reported by other workers. Ahrens (1954a) gives an average of 5 p.p.m. Cs in New England granites. The standard granite, G–1 contains 1·5 p.p.m. (Ahrens and Fleischer, 1960) which is lower than commonly encountered in spectroscopic comparisons with other granites (Ahrens, personal communication). As in the case of Li, the Cs average in granites depends on the selection of data. Late-stage granites of igneous origin are enriched in Cs. Less highly fractionated granites contain much less. Caesium is potentially a very useful indicator element for such petrological problems, in tracing the derivation of granites (Heier and Taylor, 1959). An average of 1·3 p.p.m. for five basalts is reported by Ahrens *et al.* (1960). The average K/Cs ratio in chondrites (7360) and in five basalts (7440) was found to be similar. The K/Cs ratio in more acid rocks varies widely (Ahrens and Edge, in preparation).

Canney found an average of 8 p.p.m. for Cs in sediments. Horstman reports 5 p.p.m. in shales, less than 1 p.p.m. in sandstones and an average for sediments of 4 p.p.m. Of terrestrial materials, both shales and granites are close in caesium content to the australites, although if Horstman's data is accepted, granites have significantly less caesium. Shales appear to have a rather higher concentration of Cs on the basis of either Canney's or Horstman's data. A 1:1 mixture of shale and sandstone has about 2·5 p.p.m. Cs, if Horstman's figure is used, or about 4 p.p.m. if Canney's data is used.

The Close Association of the Alkali Elements in the Australites

One of the most interesting facts to emerge from this study is the close association between all the alkali elements. This can be seen very clearly from inspection of Fig. 4, (a) to (i). All the possible cases are plotted here, and in each case, the two

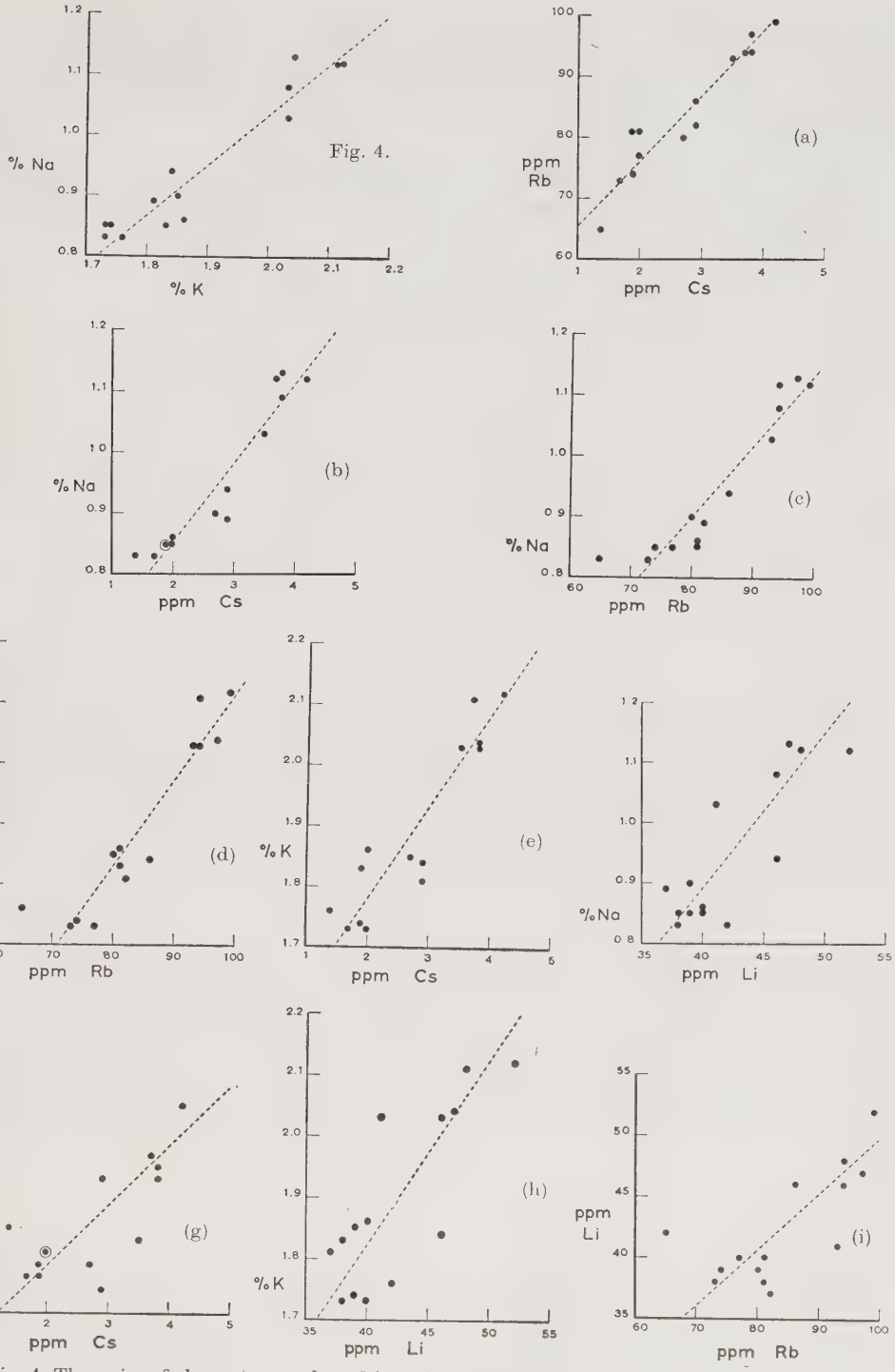


Fig. 4.

Fig. 4. The pairs of elements are plotted in order of decreasing coefficients of correlation. The close association of all pairs is evident.

elements can be seen to vary sympathetically. Thus Na–K, Na–Rb, K–Rb, Na–Li, K–Li, Na–Cs, K–Cs, Li–Rb, Rb–Cs and Li–Cs all show a coherent relationship, or positive correlation. It will be observed that the degree of association varies, and that, for example, the points show much less scatter for the pair Na–Cs than for the pair Li–Cs.

It is desirable to give a quantitative measure of the closeness of the association. A useful method is to calculate the "coefficient of correlation" (Moroney, 1956; Ezekiel, 1941). These coefficients are given in Table 8. A coefficient of +1·0 would result if all the points lay precisely on a straight line with a positive slope; that is, as x increases so does y. A coefficient of −1·0 indicates a perfect correlation with negative slope (as x increases, y decreases). A coefficient of 0 indicates no correlation at all; a completely random distribution of points. It follows that the closer the coefficient is to ±1·0, the better the degree of correlation. The coefficient (r) is given by the equation:

Table 8. Coefficients of correlation (r) for the various pairs of elements

	r
Na–K	+ 0·962
Rb–Cs	+ 0·953
Na–Cs	+ 0·952
Na–Rb	+ 0·929
K–Rb	+ 0·919
K–Cs	+ 0·916
Na–Li	+ 0·819
Li–Cs	+ 0·762
K–Li	+ 0·751
Li–Rb	+ 0·730

$$r = \frac{\Sigma[(x - \bar{x})(y - \bar{y})]}{\sqrt{[\Sigma(x - \bar{x})^2 \Sigma(y - \bar{y})^2]}}$$

where $\bar{x}$ and $\bar{y}$ are the arithmetic means of the concentrations of the two elements in question and x and y represent the individual determinations.

The significance of the coefficient of correlation can be evaluated by the "Student" t test, which indicates the probability of the correlation arising by chance for the number of samples employed. t was calculated from the equation:

$$t = \frac{r\sqrt{(n - 2)}}{\sqrt{(1 - r^2)}},$$

where n is the number of determinations and $(n - 2)$ the number of degrees of freedom. For twelve degrees of freedom, t ranges from 3·70 for the pair Li–Rb with the lowest coefficient of correlation ($r = +0{\cdot}730$) to 12·2 for the pair Na–K which have the highest coefficient ($r = +0{\cdot}962$). By reference to tables or graphs of Student's t (e.g. Fig. 81, Moroney, 1956), it is seen that for twelve degrees of freedom, a value of $t = 3{\cdot}70$ lies above the 1 per cent significance level; that is,

the correlation could arise by chance in less than one of a hundred cases, and is statistically "highly significant". The other values of t lie above the 0·1 per cent level and could arise by chance in less than one of a thousand cases.

The statistical treatment indicates that the alkali elements all show highly significant positive correlations with one another. We should remember when inspecting Fig. 4, that though the data are plotted as points, in fact each point is subject to an uncertainty which we express as the relative deviation. From the known geochemical behaviour of the alkali elements, we would predict a close coherence or association between K and Rb (Taylor and Ahrens, 1960), a weaker association of these elements with Cs, and no significant correlation with Na or Li. For the australites, we have the closest association between Na and K ($r = 0{\cdot}962$); and Rb–Cs ($r = 0{\cdot}953$), Na–Cs ($r = 0{\cdot}952$) and Na–Rb ($r = 0{\cdot}929$) are all more closely associated than the classical pair K–Rb ($r = 0{\cdot}919$).

We may briefly consider some of the implications of this strong degree of correlation between the alkali elements.

(1) Such a close coherence or association between Li, Na, K, Rb and Cs is not found in any igneous rock series. If the australites represented any sort of glassy residium from a process of igneous differentiation, it would be very difficult to account for this correlation.

(2) During weathering and sedimentation, the alkali elements tend to be widely dispersed, although K and Rb remain, in general, closely associated (Canney, 1952; Horstman, 1956).

(3) Since it is difficult to produce such associations from chemical processes, it seems possible that a physical process might produce the observed coherence. Suppose we take a homogeneous body of silicate containing the alkali elements. Let us mix with this body another mass of material, with virtually no alkali metal content. Let the mixing be not perfect, and then split up this mixture into bodies of tektite size.* We would then, on examining individual tektites, obtain sympathetic variation for all the alkali elements, such as is observed. The difference in total alkali element content of individual tektites would reflect the degree of perfection of the mixing.

The concentration of other constituents is now being determined to establish which other elements, if any, show a coherence with the alkali elements. Presumably some will show an inverse relation in composition. This data should be of much significance in setting up boundary conditions for theories of tektite origin. Thus any process invoked to explain the chemical composition of australites must not fractionate the alkali elements. These considerations will be developed more fully in a subsequent paper, when concentrations of major and many more trace elements are known.

Regional Variation in Composition

On the accompanying map of Australia (Fig. 5) are plotted the localities from which our samples come (Table 9). By comparing this with Table 1, where the analytical results are given in order of decreasing K content, it will be seen that

* The smallest recorded weight of an australite is 0·06 g, and the greatest, 218 g. Average weights for various collections range from 1 to 8·97 g. The average for all australites has been calculated as 1·5 g (Baker, 1959, p. 50).

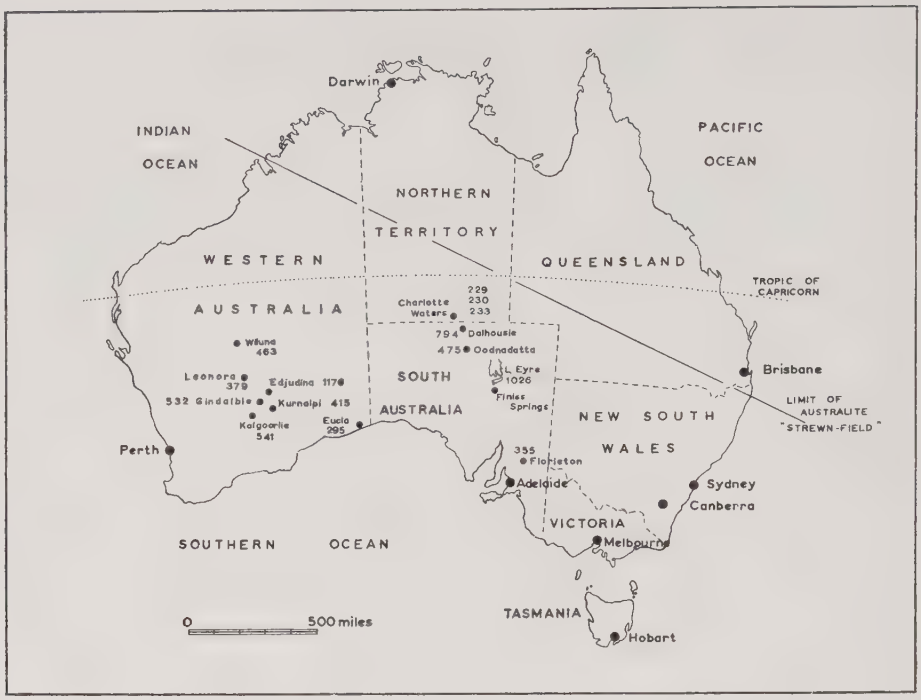


Fig. 5. Sketch map of Australia showing sample locations.

Table 9. Localities of australite specimens

No.	Locality	Collector or collection
229	Charlotte Waters and surrounding district, Central Australia	Kennett Collection
230	Charlotte Waters and surrounding district, Central Australia	
233	Charlotte Waters and surrounding district, Central Australia	
295	Near Eucla, Western Australia	E. J. Warman
355	Florieton, South Australia	Penn Collection
379	Leonora District, Western Australia	Cook Collection
415	Kurnalpi District, Western Australia	Cook Collection
463	Wiluna District, Western Australia	Cook Collection
475	Oodnadatta, South Australia	Cook Collection
532	Gindalbie, Western Australia	Cook Collection
541	Kalgoorlie District, Western Australia	Cook Collection
794	Dalhousie, South Australia	Fenner Collection
1026	Bed of East Lake Eyre, after flood	Mounted Constable Homes
1176	Edjudina District, Western Australia	B. P. Thompson

samples nos. 379, 463, 532, 541 and 1176 which have the greatest amount of K come from Western Australia, and that the South Australian samples are in general lower in alkali content. This is parallel to the decrease in refractive index observed by Baker and Forster (1943).

There are too few samples from each area to attempt the necessary statistical treatment and the writer wishes to draw attention only to the fact that the samples from Wiluna (463), Kalgoorlie (541), Leonora (379), Gindalbie (532) and Edjudina (1176) are all very similar in composition (Table 3) and contain consistently higher amounts of alkali elements than the others. In the Fig. 4, (a) to (i), they tend to form a separate cluster of points toward the top right of the diagrams. K–Cs, Na–Rb, Na–K, Li–Rb and K–Rb show this very clearly; the same grouping of these five samples shows in all diagrams. It should be mentioned that the samples were analysed in random order, and that these groupings, as well as the coherence, only became apparent after the results were obtained. Sample 415 from Kurnalpi is only a little to the east of those from Kalgoorlie and Edjudina but, with No. 295 from Eucla, which is close to the South Australian border, also resembles the South Australian samples. Unfortunately no samples from Victoria or New South Wales were available.

Acknowledgements—The writer is grateful to Miss Maureen Sachs for carrying out much of the analytical work, and for the statistical calculations. Dr. B. Daily, Curator of minerals and fossils, The South Australian Museum, kindly supplied the australite samples. Dr. C. W. Brazenor, Director, National Museum of Victoria, made available a copy of Memoir 23 of that institution. The writer is grateful to Professor L. H. Ahrens and Mr. R. D. Cherry for helpful discussions.

Acknowledgement is made to the Staff Research Fund and the Fourcade Bequest of the University of Cape Town and to the CSIR, Pretoria, for financial assistance.

References

Ahrens L. H. (1954a) The lognormal distribution of the elements. *Geochim. et Cosmochim. Acta* **5,** 49–73.

Ahrens L. H. (1954b) *Quantitative Spectrochemical Analysis of Silicates.* Pergamon Press, London.

Ahrens L. H. (1957) A survey of the quality of some of the principal abundance data of geochemistry. *Physics and Chemistry of the Earth* Vol. II, pp. 30–45. Pergamon Press, London.

Ahrens L. H. and Edge R. A. In preparation.

Ahrens L. H., Edge R. A. and Taylor S. R. (1960) The uniformity of concentration of lithophile elements in chondrites (with particular reference to caesium). In press.

Ahrens L. H. and Fleischer M. (1960) Trace element content of the standard granite (G–1) and standard diabase (W–1). *Bull. U.S. Geol. Surv.* 1113.

Ahrens L. H. and Taylor S. R. (1960) *Spectrochemical Analysis* (2nd Ed.). Addison-Wesley Press, Reading, Mass.

Baker G. (1956) Nirranda strewnfield australites, south-east of Warrnambool, Western Victoria. *Mem. Nat. Mus. Vict.* **20,** 59–172.

Baker G. (1959) Tektites. *Mem. Nat. Mus. Vict.* **23,** 313pp,

Baker G. and Forster H. C. (1943) The specific gravity relationships of australites. *Amer. J. Sci,* **241,** 377–406.

Barnes V. E. (1940) North American Tektites. University of Texas Publ. No. 3945, 477–656.

Barth T. F. W. (1952) *Theoretical Petrology.* John Wiley, New York.

Bowler C. M. L. (1959) *The Distribution of the Five Alkali Elements and Fluorine in some Granites and Associated Aureoles from the South-west of England.* D. Phil. thesis, University of Bristol.

Cabell M. J. and Smales A. A. (1957) The determination of rubidium and caesium in rocks, minerals and meteorites by neutron-activation analysis. *Analyst* **82,** 390–406.

Canney F. C. (1952) *Association of Potassium Rubidium, Caesium and Thallium in Sediments.* Ph.D. thesis, M.I.T., Cambridge, Mass.

Cohen A. J. (1959) Moldavites and similar tektites from Georgia, U.S.A. *Geochim. et Cosmochim. Acta* **17,** 150–152.

Ezekiel M. (1941) *Methods of Correlation Analysis.* John Wiley, New York.

Fairbairn H. W. (1953) Precision and accuracy of chemical analysis of silicate rocks. *Geochim. et Cosmochim. Acta* **4,** 143–156.

Goldschmidt V. M., Berman H., Hauptmann H. and Peters Cl. (1933) Zur Geochemie der Alkalimetalle. *Nachr. Ges. Wiss. Göttingen* Kl. III, **34,** Kl. IV **35,** 235–244.

Harrison G. R. (1939) *M.I.T. Wavelength Tables.* John Wiley, New York.

Heier K. S. and Taylor S. R. (1959) The distribution of Li, Na, K, Rb, Cs, Pb and Tl in southern Norwegian pre-Cambrian alkali feldspars. *Geochim. et Cosmochim. Acta* **15,** 284–304.

Herzog L. F. and Pinson W. H. (1956) Rb/Sr age, elemental and isotopic abundance studies of stony meteorites. *Amer. J. Sci.* **254,** 555–566.

Horstman E. L. (1956) The distribution of lithium, rubidium and caesium in igneous and sedimentary rocks. *Geochim. et Cosmochim. Acta* **12,** 1–28.

Moroney M. J. (1956) *Facts from Figures* (3rd Ed.). Pelican, London.

Pinson W. H., Ahrens L. H. and Franck M. L. (1953) The abundances of Li, Sc, Sr, Ba and Zr in chondrites and some ultramafic rocks. *Geochim. et Cosmochim. Acta* **4,** 251–260.

Pinson W. H., Herzog L. F., Fairbairn H. W. and Cormier R. F. (1958) Sr/Rb age study of tektites. *Geochim. et Cosmochim. Acta* **14,** 331–339.

Pinson W. H. and Schnetzler C. C. (1959) Chemical and physical studies of tektites. *Bull. Geol. Soc. Amer.* **70,** 1656. (Abstract.)

Shaw D. M. (1954) Trace elements in pelitic rocks—I. Variation during metamorphism. *Bull. Geol. Soc. Amer.* **65,** 1151–1166.

Strock L. W. (1936) Zur Geochemie des Lithiums. *Nachr. Ges. Wiss Göttingen* Kl. IV, N.F. 1, No. 15, 171–204.

Taylor S. R. (1954) *Geochemistry of Some New Zealand Igneous and Metamorphic Rocks.* Ph.D. thesis, Indiana University, Bloomington, Indiana, University microfilms 7546.

Taylor S. R. (1960) Occurrence of alkali metals in some Gulf of Mexico sediments: Amended rubidium values and K/Rb ratios. *J. Sed. Petrol.* In press.

Taylor S. R. and Ahrens L. H. (1959) The significance of K/Rb ratios for theories of tektite origin. *Geochim. et Cosmochim. Acta* **15,** 370–372.

Taylor S. R., Emeleus C. H. and Exley C. S. (1956) Some anomalous K/Rb ratios in igneous rocks and their petrological significance. *Geochim. et Cosmochim. Acta* **10,** 224–229.

Taylor S. R. and Heier K. S. (1958a) Alkali elements in potash feldspars from the pre-Cambrian of Southern Norway. *Geochim. et Cosmochim. Acta* **13,** 293–302.

Taylor S. R. and Heier K. S. (1958b) Rubidium depletion in feldspars. *Nature, Lond.* **182,** 202–203.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 101 to 114. Pergamon Press Ltd. Printed in Northern Ireland

Rare gases in tektites*

J. H. Reynolds
Department of Physics, University of California
Berkeley, California

(*Received* 18 *September* 1959)

Abstract—Tektites from a number of localities have been examined for their contents of potassium, atmospheric argon, radiogenic argon, atmospheric neon, and possible cosmogenic neon. At 300°K, the coefficient of diffusion for helium in tektite glass from Kalgoorlie, Australia is 4×10^{-10} cm²/sec. The activation energy for helium diffusion is 0·27 electron volts. The helium solubility constant is 0·005. Corresponding quantities for neon diffusion are 2×10^{-15} cm²/sec, 0·61 electron volts and 0·005. The helium diffusion rate is so high that tektites retain no radiogenic or cosmogenic helium. The recent group of tektites, however, should retain a substantial amount of any cosmogenic neon contained at time of fall. In no case was any excess Ne^{21} detected. From the upper limits of original Ne^{21} content, a maximum "flight time" since last melting has been computed for each tektite. For a tektite from Kalgoorlie, this is 28,000 years. This result is in apparent disagreement with the finding by Ehmann and Kohman of radioactive Al^{26} in australites. Potassium–argon ages have been computed for each tektite. These range from 0 to 32 m.y. and are usually in agreement with the stratigraphic age of the formations on which the tektites lie, according to presently accepted time scales. Data in this paper do not support a recent suggestion that the moldavites of Czechoslovakia and the recently discovered tektites from Georgia, U.S.A. are part of the same fall.

Introduction

Tektites are curious pieces of dark glass which are found in scattered locations all over the world. For a variety of reasons—e.g. shape, distribution, evidence in the australite "button-form" for two distinct periods of melting, and absence of any plausible terrestrial origin—it has long been accepted that they fell from the sky. Keen interest in these objects accounts for a substantial and rapidly growing literature on the subject as various modern analytical techniques are applied. (See, for example, the papers of the 1957 Symposium on tektites, published in *Geochimica et Cosmochimica Acta*, Vol. 14, No. 4, October, 1958).

Tektites contain about 2 per cent potassium. It is not surprising, then, that among the earliest experiments in potassium–argon dating were attempts to date these objects. It was immediately established (Suess, Hayden, and Inghram, 1951 and Gerling and Yashchenko, 1952) that tektites are not very ancient objects like the meteorites. The first of these papers placed upper limits of 10 m.y. and 32 m.y. on the age of a philippinite and an australite, respectively; the second, placed upper limits of 12 m.y., 5 m.y. and 3 m.y. on the ages of a rizalite (Philippine Islands), an indochinite, and a moldavite. These results, while important, are not very precise. There have been substantial refinements since 1951 in techniques for K–A dating. One of the reasons for undertaking the work reported in this paper was to apply modern K–A dating methods to the tektite problem with hopes of obtaining more detailed age data.

Another interesting question is whether or not cosmogenic isotopes, i.e. nuclides produced in spallation reactions due to cosmic ray bombardment, occur in tektites. Meteorites are now known to contain He^3, He^4, Ne^{20}, Ne^{21}, Ne^{22}, A^{36} and A^{38} as a result of cosmic-ray bombardment during their flights in space. In meteorites.

* Work supported in part by the U.S. Atomic Energy Commission.

these isotopes are usually present in amounts measurable by modern mass spectrometric techniques. Among these isotopes those of helium and neon should also be produced in tektites. It seemed profitable, then, to investigate tektites for possible Ne^{21} and He^3 content, since the mass spectrometric detectability for these two isotopes is high enough so that results of not too many thousands of years of unshielded cosmic-ray action should be detectable. It was recognized from the start that helium and neon can migrate through glass by diffusion. Rates for these processes would therefore have to be established before any helium or neon data could be interpreted. Diffusion studies for these gases were therefore planned.

After these searches for stable cosmogenic isotopes had begun, it was learned that Ehmann and Kohman (1958) had detected Al^{26} activity, presumably cosmogenic in origin, at a level similar to that in a stone meteorite, in australite glass from Kalgoorlie, Western Australia. This result was strengthened by their finding no Al^{26} activity in a bediasite and in a moldavite. (These last tektites are associated with Eocene and Miocene formations, respectively, and should have lain on the earth since their fall for a time sufficient for the Al^{26} activity to decay to undetectable levels.) These experiments of Ehmann and Kohman seemed conclusively to establish an extra-terrestrial origin for tektites and required, at least in the case of the australites, a "flight-time" of the order of several hundred of thousands of years for the Al^{26} activity to build up to meteoritic levels.

The work reported in this paper was begun during the summer of 1958 in collaboration with G. C. Ford who was then visiting Berkeley. Preliminary results were reported (Reynolds and Ford, 1959) at a meeting of the American Physical Society.

Experimental Methods

Diffusion studies. Diffusion coefficients were determined by a technique similar to that used by Gentner and Trendelenberg (1954) in their studies of helium diffusion in alkali halides. About three grams of 100 to 150 mesh tektite glass from Kalgoorlie, Australia (sample KA 353) was "conditioned" by saturating it with He^3 and Ne^{22} in the following manner. The sample, in a copper thimble fitted with a Kovar to Pyrex seal, was attached to a small Pyrex manifold together with unopened ampoules of He^3 gas (0·085 cc STP) and neon enriched to 50% Ne^{22} (0·030 cc STP). The manifold was pumped and baked at 350°C overnight. Next morning the pressure as indicated on an ion gauge was 5×10^{-9} mm. The manifold was sealed off from the pumps and the ampoules broken open. The copper thimble was then heated to 580°C and maintained at this temperature for 18 hours. The total volume of the system with ampoules opened was 41 cc. The Kovar tube between the copper thimble and the Pyrex system was water cooled so that the only hot glass to which the gases were exposed were the sample grains. Subsequent determination of the diffusion rate for neon in the glass at 580°C indicated that both gases were in solution equilibrium with the glass after the 18 hour heating.

Immediately after this "conditioning" of the sample, most of the glass powder was transferred to a new copper thimble which was then attached to the Pyrex sample manifold of a highly outgassed mass spectrometer (Reynolds, 1956) along with a finger containing 8·5 grams of activated charcoal. This system was pumped overnight while heating the charcoal finger but not the sample. On the next day heating of the sample in the copper thimble was begun, the expelled gas for each temperature being collected in the isolated volume of the sample system. After each heating period, the gas evolved was expanded into the mass spectrometer tube after first closing the pump valve for the mass spectrometer so that the spectrometer served as a He^3- and Ne^{22}-sensitive manometer. During measurement the charcoal finger was chilled with liquid nitrogen so as to absorb any chemically active gases which might interfere with the measurements.

The heating program and Ne^{22} peak-height data are to be found in Table I. No He^3 peaks were observed except a trace peak after the first heating, indicating that the preliminary pumping at room temperature overnight had been sufficient to expel most of the helium from the glass. At the conclusion of the heating program outlined in Table 1, a neon spike which had been calibrated by isotope dilution was opened in the same sample system-mass spectrometer enclosure so as to calibrate the mass spectrometer for neon. Such a calibration is unnecessary for the determination of the diffusion coefficients, but permits an evaluation of the neon solubility in the tektite glass.

Table 1. Neon diffusion data

Temp (°C)	Time (hr)	Ne^{22} released (in chart divisions)	Fraction of Ne^{22} remaining in sample
110	16·0	62	0·9352
200	3·2	125	0·8047
300	2·7	360	0·4287
350	2·1	200	0·2198
400	2·1	140	0·0736
450	1·8	58	0·0130
580	1·4	12·5	0
Total		957	
Spike NA29 ($1·8 \times 10^{-6}$ cc STP Ne^{22})		4000	

Table 2. Helium diffusion data
(Values in parentheses are computed values)

Temp (°C)	Time (hr)	He^3 released (in chart divisions)	Fraction of He^3 remaining in sample
20	0·20	(4500)	0·695
−78	49·5		
20	3·0	6400	0·2612
−78	22·4	(68)	0·2566
50	1·25	2170	0·1096
−78	15·5	29	0·1076
100	1·75	1370	0·0147
165	1·25	184	0·0022
255	1·7	34	0
Total		14755	
Spike HA9 ($3·8 \times 10^{-7}$ cc STP He^3)		1160	

A second run was necessary to obtain the desired helium data. For this run the tektite glass was "conditioned" in a He^3 atmosphere for 18 hours at 300 C—this temperature being adequate for dissolving helium. Immediately upon being transferred to a fresh copper thimble for the mass spectrometer measurements, the sample was chilled to −78°C with dry ice and was kept chilled in this way except when sample heating was in process. Even at dry ice temperature there is measurable migration out of the glass, but a correction was subsequently applied for He^3 lost during pumping at −78°C. The helium data are presented in Table 2.

Tektite studies. Tektite specimens were crushed in a diamond mortar until all material was reduced below 20 mesh. The 20–150 mesh fraction was used for the rare-gas analysis; the minus 150 mesh fraction was used for potassium analysis. Tektites are virtually a pure glass (we

have seen no X-ray lines in samples X-rayed) so that there should be no significant error in sampling them in this way.

Potassium analyses reported in this paper are by flame photometry using a Beckman Model DU flame spectrophotometer. Two completely distinct determinations were made on each sample. For every eight unknown samples processed, one National Bureau of Standards standard sample was run. Agreement between paired determinations and between N.B.S. values and flame photometer values was always within a few per cent of the value found. Neon and argon samples were extracted in the apparatus shown in Fig. 1. With the apparatus

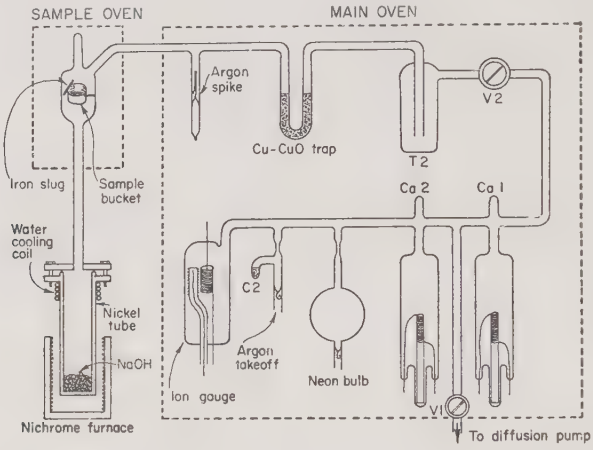


Fig. 1. Cu-CuO trap fabricated from Corning 1720 glass. All other glass is Pyrex. T2: liquid nitrogen trap. V1, V2: Alpert all-metal bakeout vacuum valves. C1 (not shown): an activated charcoal finger between V2 and Ca1. C2: activated charcoal finger for removal of argon. Ca1, Ca2: calcium furnaces. Calcium turnings are in stainless steel thimble within platinum helix wound on grooved quartz. Ca1 is reused until it fails. Ca2 is a standby furnace.

assembled as shown, the following preliminary bake-out temperatures were used: main oven—350°C, sample oven—200°C, nickel furnace—600°C. After bake-out the pressure was measured with the ion gauge. The run was not continued until the pressure was less than 2×10^{-8} mm with V1 and V2 open and with liquid nitrogen on trap T2.

When this degree of vacuum was attained, V2 was closed, the sample was dumped onto the now cold NaOH cake, the calibrated A^{38} "spike" was broken open, and heating power was gradually applied to the nickel furnace with a motor-driven Variac. The NaOH temperature was brought to 600°C within about eight hours and kept at this value for at least eight hours more. Purification of the released gases was then accomplished by first drawing the gases into C1 through the Cu–CuO trap (550°C) and through T2 (liquid nitrogen temperature) and then closing V2 and treating the gas released from C1 with calcium vapor from one of the calcium furnaces. Finally, purified argon was drawn into take-off C2 and purified neon was removed in the 500 cc bulb, that volume comprising about 25 per cent of the total volume of the system.

A blank run in which all these steps were executed, except for dumping a tektite sample, resulted in an atmospheric argon sample of $0{\cdot}65 \times 10^{-6}$ cc STP. The typical yield of atmospheric argon from a tektite sample was 15 times as large. No neon blanks were run. However if blank neon amounts to that associated in the atmosphere with the argon blank, the neon blank is less than that from tektite samples by a factor of about 2000.

Yields of atmospheric and radiogenic argon were computed from the isotopic composition of the "spiked" mixture. Yields of neon were usually determined ("B" determinations) by introducing the entire sample into the closed-off mass spectrometer and using the machine as a peak-height manometer which was then calibrated immediately by adding a Ne^{22} spike. This calibration was found to be constant enough (within about 20 per cent) over long periods so that in some of the later runs ("C" determinations) the average calibration factor was assumed and

not measured. In a few other cases—where the tektite neon sample was sufficiently large—the isotopic composition of the sample-spike mixture within the mass spectrometer was used to calculate the neon yield by isotope dilution. In all such cases ("A" determinations) the "manometer method" and the "isotope dilution method" gave concordant results. In Table 3, the neon data are labeled A, B, or C according to the method of measurement used.

Experimental Results

Diffusion studies. Diffusion constants were calculated from the data in Tables 1 and 2, assuming for a model the isotropic diffusion from spherical particles in which the gases were initially uniformly dissolved. An average particle radius of 65 microns was calculated by weighing 200 of the 100–150 mesh particles, which are reasonably equant. In this calculation a value of 2·47 (Summers, 1913) was taken for the specific gravity of Kalgoorlie australite glass.

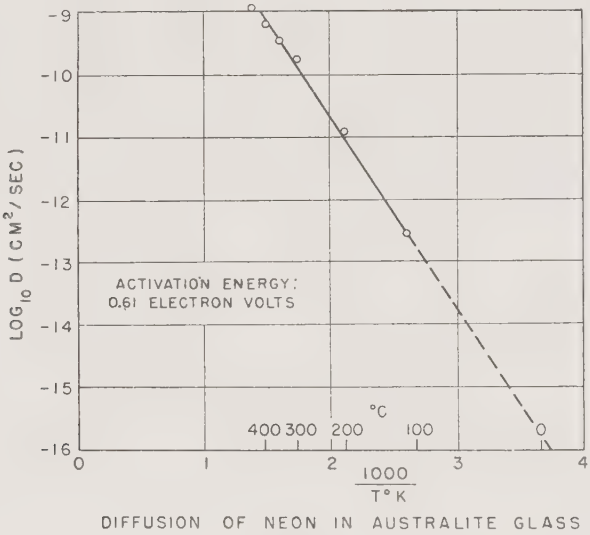


Fig. 2.

The neon calculation was straightforward. The helium calculation, however, was complicated by the escape of unknown amounts of He^3 during sample transfer at room temperature and during pump-out at −78°C. Since data were taken for "heatings" at these two temperatures, a method of successive approximations could be used to find a diffusion curve consistent with the data.

The diffusion coefficient for neon is plotted logarithmically versus the reciprocal temperature in Fig. 2. Within experimental error the curve can be fitted by a single straight line on this plot with slope corresponding to an activation energy of 0·61 electron volts. The lowest temperature heating was at 110°C so that a room temperature value can be obtained from these data only by extrapolation. There results for t = 27°C the value $D = 2 \times 10^{-15}$ cm²/sec. The data also permit evaluation of the solubility constant of neon in tektite glass. This quantity, S, can be defined as the equilibrium ratio of the volume density of neon atoms in the glass phase to that in the gas phase. We find that for neon at 580°C, $S = 0{\cdot}005$.

The diffusion coefficient for helium is plotted in Fig. 3. While the low temperature points are on a straight line, the two high temperature points deviate from this line. If the straight line correctly represents the helium diffusion coefficient, the amount of helium which was collected after the 100°C heating is that which would be expected, but the amounts collected after the 165°C heating and the 255°C heating should have been essentially zero. It appears possible that these traces of He^3 may have been part of the He^3 which redissolved in some of the room-temperature Pyrex of the sample system at a time when gross quantities were being expelled

from the sample. If so, this He^3 was collected during the final heatings from a *secondary* source and is spurious. No attempt was made to confirm this hypothesis because the room temperature value of the helium diffusion coefficient—which is the important datum for our purposes—lies on the undisputed portion of the curve. Its value is 4×10^{-10} cm²/sec. The slope of the straight line portion corresponds to an activation energy of 0·27 electron volts. The solubility constant of helium in tektite glass at 300°C was found to be, again, 0·005.

Tektite studies. The analytical results for the tektites are collected in the first 13 columns of Table 3. The tektites are arranged in order of increasing indicated K–A age. The first three columns give the type, approximate location, and Berkeley sample number. More detailed descriptions of samples and sample localities will be found in a later section. The weight in

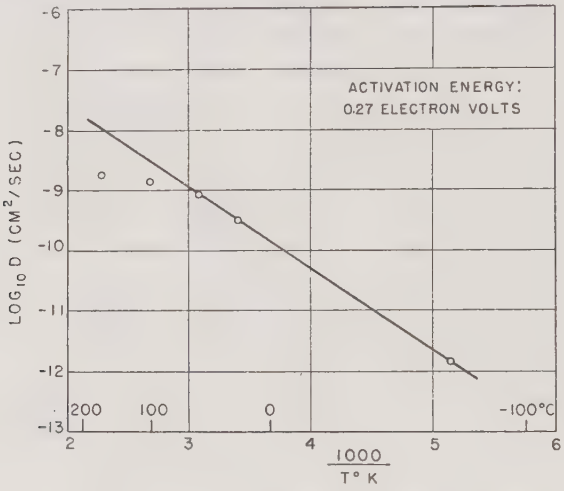


Fig. 3.

column 4 refers to the sample taken for rare-gas analysis. Column 5 contains the result of the potassium analysis—judged to be accurate within 2·5 per cent. The duration of the 200°C pre-heating of the sample is recorded in column 6. These times are variable since several bakings of the extraction system were sometimes needed before vacuum problems were overcome.

The radiogenic—A^{40} to K^{40} ratio is listed in column 7. The indicated K–A ages appear in column 8, together with the assigned analytical errors. The potassium decay contents are those currently adopted* by Aldrich and Wetherill (1958). No duplicate determinations were made of K–A ages since it was believed to be more important, at this stage, to extend the tektite survey rather than to confirm individual results. There are, however, two K–A age determinations for Kalgoorlie australites, using different specimens. The determination on sample KA-352-1 was made near the beginning of the study when it was still thought possible that helium extracted from the tektites would be of some value. Accordingly the sample was given no pre-heating, which may account for the fact that this specimen is richer in atmospheric argon than any other of the young group of tektites. This determination also differs from the others in that no argon spike was added until after the argon sample had been examined in the mass spectrometer. Incomplete recovery of the argon sample would, in this instance only, result in an excessively young K–A age for the specimen. The difference between the $0{\cdot}44 \pm 0{\cdot}2$ m.y. and the $0{\cdot}80^{+0{\cdot}5}_{-0{\cdot}2}$ m.y. ages found for the two Kalgoorlie samples may be due to analytical error or may be real—further work would be needed to decide. It may be significant that the sample giving the younger age was a composite sample consisting of 3 small tektites, whereas that giving the older age was a single, large tektite.

* $\lambda_k = 0{\cdot}585 \times 10^{-10}\,\mathrm{yr}^{-1}$; $\lambda = 5{\cdot}30 \times 10^{-10}\,\mathrm{yr}^{-1}$.

Table 3. Results of tektite analyses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Sample Type	Sample Location	Sample No.	Sample Weight (g)	$^{o}_{o}$K	Preheat (200°C) (time hr)	$\frac{(A^{40})R}{K^{40}} \times 10^4$	K-A Age, m.y.	$^{o}_{o}$ Atmos. Argon	Atmos. Argon/g, 10^{-7} cc/g	Atmos. Neon/g, 10^{-9} cc/g	Excess Ne^{21}/g, 10^{-11} cc/g	Neon (how determined)	Neon (retained before preheat)	Neon (retained after preheat)	Max. flight time (m.y.)
Rizalite	Phillipine Islands	KA 377-1A	11·3	2·02	71	(−0·05)	$<0·3$ ($-0·09 \pm 0·3$)	>99	16·9	0·17	<1·1	C	>0·59	>0·44	0·040
Australite	Kalgoorlie, W. Australia	KA 357-1	12·2	1·95	18	0·26	0·44 ± 0·2	93·7	5·1	Lost	Lost	Lost	—	—	—
Tektite	Central Sumatra	KA 360-2	7·5	1·76	61	0·29	0·50 × 0·2	96·6	10·2	0·49	<1·3	B	0·087	0·067	0·31
Tektite	Tan Hai, China	KA 376-1B	11·4	2·13	29	0·46	0·79 ± 0·2	87·0	4·5	2·5	<9	C	0·37	0·31	0·46
Australite	Kalgoorlie, W. Australia	KA 352-1	27·1	2·00	0	0·47	$0·80^{+0·5*}_{-0·2}$	95·6	14	1·6	<0·84	A	0·49	0·49	0·028
Moldavite	Bohemia (?)	KA 359-1	8·7	2·78	17	7·93	13·5 ± 0·4	50·9	14	0·37	<1·9	B	0·019	0·017	1·8
Bediasite	Lee County, Texas	KA 355-4	5·6	2·12	18	17·1	29·0 ± 0·9	53·0	28	2·2	<2·8	C	~0	~0	∞
Empirite	Empire, Georgia	KA 375-1B	5·0	2·04	16	18·8	32·0 ± 1·0	19·8	6·5	2·7	<14	C	~0	~0	∞
Argon Blank			16·3		20			100	0·65†						

* Sample spiked in mass spectrometer.
† For assumed 10 g sample.

The extent of contamination of the radiogenic argon by atmospheric argon is entered in columns 9 and 10. The content of atmospheric argon is reasonably uniform, ranging from 4 to 28 $\times$ 10^{-7} cc STP per gram. There is no clear-cut correlation between argon content and sample age or sample size. Columns 11 and 12 contain the neon data. The content of atmospheric neon per gram ranges from 0·2 to 2·7 $\times$ 10^{-7} cc STP, exhibiting about the same spread—or lack of it—as the atmospheric argon data. Upper limits on the excess Ne^{21} content are listed in column 12. In no case was any excess Ne^{21} found which could be considered real. There was an apparent excess in the Empire, Georgia sample and the Tan Hai, China sample but in neither case was the result significantly above experimental error. Column 13 describes the technique used in determining the amount of atmospheric neon, as discussed earlier. The most reliable technique (isotope dilution) is labeled A; the less reliable techniques (spectrometer peak height with and without immediate calibration) are labeled B and C respectively.

Discussion

Diffusion results

The use, in the diffusion experiments, of dissolved gases which are isotopically different from the atmospheric forms is a powerful technique in that there is no danger that the results will be influenced by contamination. The method is very sensitive for the same reason. The values found appear very reasonable in view of the following discussion.

The diffusion coefficient, heat of diffusion, and solubility found for helium in tektite glass agree in general with published values for laboratory glasses, For example Rogers, Buritz, and Alpert (1953) find for helium in Pyrex glass values of $S = 0{\cdot}0065$, *activation energy* $= 0{\cdot}28$ electron volts, and $D = 4{\cdot}8 \times 10^{-4}$ which may be compared with $S = 0{\cdot}005$, *activation energy* $= 0{\cdot}27$ and $D = 0{\cdot}2 \times 10^{-4}$ for the tektite glass. The lower diffusion constant for the tektite glass than for Pyrex agrees with the observation (Norton, 1957) that the helium permeation rate increases with the weight percent of "glass-formers" (SiO_2, B_2O_3, P_2O_5). If the solubility constant is assumed to be the same at 100°C as at 300°C, the helium permeation velocity can be computed and plotted on Norton's curve of permeation velocity *versus* weight per cent glass-formers. The permeation rate appears to be greater by about a factor of ten than that expected from Norton's curve for a glass of 74 per cent silica content (the SiO_2 percentage for this sample according to an analysis by D. Tilles of this laboratory). Or, in other words, the helium permeation rate for tektite glass corresponds to that expected from Norton's curve for a glass of about 85 per cent silica content. This is certainly not a serious discrepancy.

Norton also publishes a single datum for the neon permeation rate in pure silica: at 700°C he finds this to be 4·2 $\times$ 10^{-10} in units of cc gas STP per sec per/cm^2 area per mm thickness per cm of gas pressure. From the data in this paper, again assuming the solubility of 0·005 to be temperature insensitive, the neon permeation rate in tektite glass would be 0·13 $\times$ 10^{-10}. Again the difference is in the direction which suggests that the permeation rate is depressed by the presence of non glass-formers.

Helium and neon losses by the tektites

As may be seen from a study of the sample descriptions in a later section, the "flattish" tektites used in this study had a mean thickness of about 1 cm; the

"chunky" tektites had a mean radius of 1 cm. In both a plate and a sphere the diffusion loss becomes, in time, exponential. For the sphere, the half-life for diffusion loss is very nearly equal to $a^2/14D$ where a is the radius and D is the diffusion coefficient. As a first step in considering diffusion loss it is instructive to compute this quantity using 1 cm as the radius and those values of D found for helium and neon in a tektite at room temperature. We find for helium diffusion a half life of 5·6 years; for neon diffusion, a half life of 1·1 million years.

It is immediately clear from the helium value that any cosmogenic helium dissolved in the tektite at the time of fall will have long since been "flushed-out" with helium from the atmosphere of the earth—since all tektite specimens are "finds" and none are "falls". The characteristic time for neon loss is, on the other hand, a great deal longer.

We are concerned with two types of neon loss. First there occurs neon loss between the time of fall and the time of assay. This has been computed for each specimen in Table 3 assuming that the K–A age gives us correctly the time since fall, and assuming that the temperature has been uniform at 300°K. The shapes were idealized to plates or spheres, whichever was the more appropriate. In column 14 appears the fraction of the original neon which would remain after this initial loss. Second, there is a small amount of neon loss during the preliminary sample bake-out at 200°C. Here the particles are roughly spherical with an average radius of about 200 microns. In column 15 appears the fraction of the original neon remaining after this second loss. Division of the upper limit of excess Ne^{21} content by this overall retention factor gives us an estimate of the original Ne^{21}, or its upper limit.

Maximum flight times for the tektites

It is possible to estimate the production rate of Ne^{21} while the tektite is in space. Schaeffer and Fisher (1959) have measured the cross section for the production of Ne^{21} in aluminum by 700-MeV protons. Their value of 21 millibarns can probably be applied also to silicon, magnesium, and sodium for the purposes of rough calculation. An omnidirectional flux of 3 primary cosmic ray particles per cm^2 per sec is assumed (Meredith, Van Allen, and Gottlieb, 1955). The tektites are small objects so that there is presumably no shielding correction to be applied.

Column 16 of Table 3 contains the upper limit for the flight time calculated in this way. The neon losses estimated in the last section have been included. For most of the old tektites, these losses have been severe and very little can be said about the flight time. Even for the young tektites, the maximum flight time is usually not very much less than the K–A age. However, for one specimen from Kalgoorlie, W. Australia, the maximum flight time of 28,000 years is substantially less than the K-A age. For a Philippine tektite, the maximum flight time is 40,000 years. Minimum flight times are, of course, zero for all cases. These data appear to require that tektites arrive at the earth fairly promptly after their last melting.

As mentioned earlier, Ehmann and Kohman (1958) have detected substantial amounts of Al^{26} activity in a tektite from Kalgoorlie, Australia. Their result

indicates a flight time not much less than the Al^{26} half-life of 800,000 years—otherwise the Al^{26} cannot build up to a meteoritic level. Kohman (private communication, 1959) now writes that some doubts have arisen concerning the Al^{26} work and that the measurements are being extended. Meanwhile the discrepancy would require a severe heating of the Kalgoorlie tektites subsequent to their flight so that Ne^{21} has been expelled but not Al^{26}.

The K–A ages

The Pacific Ocean area tektites, usually described as recent, have K–A ages ranging from 0 to 0·8 m.y. in agreement with this geological classification. Among these, the Philippine specimen at 0·3 m.y. appears to be the youngest and one of the Kalgoorlie tektites at 0·8 m.y., the oldest. A discrepancy between runs on two samples of Kalgoorlie material has been discussed earlier. However the errors in the determinations (about 0·2 m.y.) are such that very little importance can be attached to age differences within the group. The large errors arise from the large amounts of contamination of the radiogenic argon in the tektites by atmospheric argon (87 to >99 per cent). To increase the accuracy of these determinations would require one of two possible approaches. If considerably larger samples were used, the isotope ratio A^{36}/A^{40} could be determined with more precision. Present probable errors of one per cent in the 36/40 ratio could probably be reduced to 0·2 or 0·3 per cent by this approach, with a proportionate reduction in final error. The other possibility would be to try to reduce the level of contamination of the samples by judicious pre-heating. Evernden, Curtis, and Kistler (1957) have found that by preheating Pleistocene volcanic sanadine at 500° for 48 hours prior to the main argon extraction, they can reduce the atmospheric contamination level by a large factor without appreciable loss of radiogenic argon. It may be possible to find a successful preliminary treatment for tektite glass also.

Turning to the older specimens, Janoschek (Barnes, 1940) considers that the moldavites are middle Miocene in age. Evernden (1959) in describing a time scale based on K–A dating work at Berkeley estimates that the Miocene extends from 12 to 26 m.y. so that the value found for the Bohemian moldavite of 13·5 m.y. is in fair agreement with current time scales. Burial at depth could expose the tektites to elevated temperatures, accelerate argon loss, and lead to a young age. The "grain-size" for argon diffusion in tektites is large, favoring retention, but the diffusion coefficient for argon in glass is no doubt much larger than in crystalline media so that argon loss can be expected at depth. For this reason, K–A ages of ancient tektites should probably be interpreted as lower limits. In this sense there is little discrepancy in the moldavite result.

The Texas bediasites are usually found resting on rocks of the Jackson group of formations from which they are believed to be weathering. These formations are of late Eocene age—35+ m.y. according to Evernden. Thus the K–A age of 29·0 m.y. is again not far from current estimates of the stratigraphic age and again deviates in a direction which could be explained by argon loss.

The Georgia tektites are found on the surface (not *in situ*) of the Hawthorn formation of middle or lower Miocene age (Cook, 1943). In this case, then, the K–A age of 32 m.y. is older than the upper limit of 26 m.y. put on the Miocene by

Evernden. Dr. Virgil E. Barnes who has visited the tektite localities in Georgia comments as follows. "Georgia tektites rest on the Hawthorn formation and very likely are weathering out of this formation; however, the Hawthorn formation is coastward from nearby Oligocene rocks and it is possible that the tektites could have weathered out of these rocks, or even out of Eocene rocks, and could have been transported to where they are now found". Also, in reading the published description of the Hawthorn formation, one notes that the formation is sparse in fossils and infers that there is not strong fossil control on the age of the parts of the formation containing the tektites.

Cohen (1959) has pointed out a number of similarities between the moldavites and tektites from Georgia, U.S.A. and suggests that they may form parts of the same fall. The age determinations in Table 3 certainly do not support this suggestion. In this connection, attention may also be drawn to the anomalously high potassium content of 2·78 per cent found for the Bohemian moldavite. No other tektites we have examined, including the Georgia specimen, have potassium percentages higher than 2·1.

Acknowledgements—This work was supported in part by the U.S. Atomic Energy Commission.

I am grateful to Dr. G. C. Ford for assistance in the early work on the problem and to Dr. D. Krummenacher for assistance on the experimental work on the rizalite. I wish to express my appreciation to Mr. L. Kovich for his painstaking work on the potassium analyses. The work was completed during a time when I held a fellowship in The Miller Institute of Basic Research, University of California.

I am grateful to Prof. T. P. Kohman of the Carnegie Institute of Technology for the moldavite specimen and to Prof. J. A. S. Adams of the Rice Institute for the bediasite. Thanks are due to Dr. A. J. Cohen of the Mellon Institute for a pre-publication copy of his paper and for the suggestion that the work include a study of Georgia tektite. The Sumatra tektite fragments were presented to Prof. J. Evernden of this university by Prof. G. H. R. Von Königswald of the University of Utrecht, to both of whom I am grateful.

Finally I cannot exaggerate the helpfulness to me and others engaged in tektite research of Mr. E. P. Henderson of the Smithsonian Institution, U.S. National Museum, Washington, D.C. who has worked to see that tektites have been made available to qualified research people without at the same time endangering the completeness of museum collections. The specimens from Australia, China, the Phillipine Islands and Georgia, U.S.A. are all from the U.S. National Museum collections.

Note added in press

W. Gentner and J. Zähringer very kindly sent me a copy of their preliminary results on the dating of tektites* together with the comment that in their experiments contamination by atmospheric argon was typically only 10^{-8} cc STP/g as opposed to our values of about 10^{-6} cc STP/g. Since in our work blank runs showed that most of the contamination came from the samples, it was immediately clear that in some manner our specimens were becoming contaminated to a degree very much greater than those studied by Gentner and Zähringer. We thus investigated the possibility that our contamination arose as a result of crushing the samples and exposing the fresh glass surfaces to the atmosphere for a considerable time before treating the samples in the extraction apparatus.

* W. Gentner and J. Zähringer (1959) Kalium-Argon-Alter einiger Tektite, Zeit. für Naturforsch. 14a, 686–7.

Suppose that at time $t = 0$, a fresh sphere of glass (radius a) is exposed to an atmosphere of argon, the diffusion coefficient being D_1. At time $t = t_1$, the sphere is transferred to a heated vacuum system where the diffusion coefficient is D_2. Suppose that $D_1 t_1 \ll D_2 t_2 \ll a^2$. Then at the end of the heating, the residual atmospheric argon content is given by

$$\frac{Q}{Q_{sat}} = \frac{3\ D_1 t_1}{\sqrt{\pi}\, a \sqrt{D_2 t_2}}$$

where Q_{sat} is the amount of argon which would be taken up in the sphere for $t_1 = \infty$.

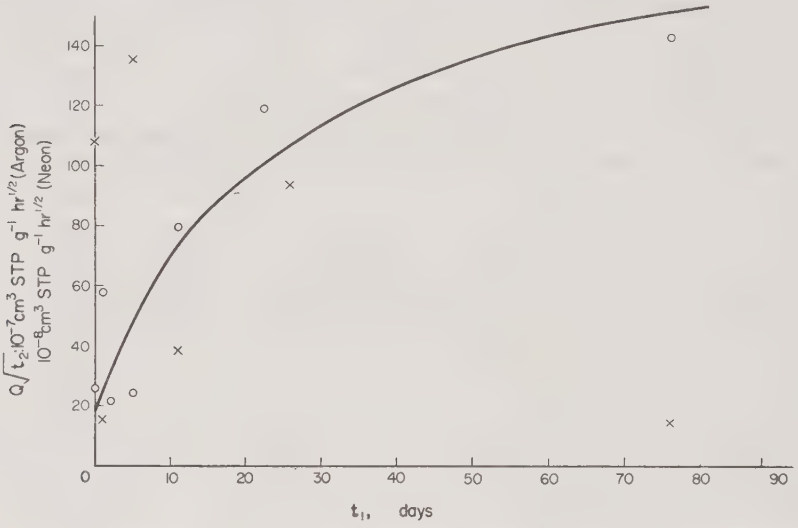


Fig. 4. Atmospheric gases in crushed tektites; t_1: soak-up time, t_2: bake-out time. O—argon, X—neon.

Fortunately we had kept records of the time interval between crushing and heating for every specimen in Table 3 except for sample KA 352-1 which was crushed on an unknown date. These times in the order of Table 3 are 76, 2, 11, 5, —, 1, 26, and 0 days. If the above model is correct, a plot of $Q\sqrt{t_2}$ versus t_1 should be a straight line through the origin. This plot appears in Fig. 4. It will be noted that the argon data can be fitted quite well by a smoothly ascending curve. It is not a straight line, to be sure, but the plot systematizes the previously random contamination data in such a way as to suggest that the model has correct features. The much less precise neon data have also been plotted. Here the points scatter badly.

It is surprising that the degree of residual contamination is so severe after a 200° bakeout. However, Q_{sat} may be very high for fresh tektite glass, in which the initial gas content is evidently very low, when exposed to the atmosphere since argon would be the first gas molecules to migrate into the voids in the tektite.

Gentner and Zähringer have subsequently sent us a more complete account of their experiments in which they state that their samples were not crushed, as we had inferred. Because of the low contamination in their experiments the precision of their ages on young tektites is very much greater than those in this

paper. Within quoted errors however, the two studies are in agreement. I wish to thank Professor GENTNER and Dr. ZÄHRINGER for letting me see their results prior to publication.

DESCRIPTIONS OF THE SAMPLES

The idealized sizes and shapes used in the calculation of neon loss during geological history are listed in parentheses

KA 352 Kalgoorlie, Western Australia, from Lot 1, U.S. National Museum collection, single tektite, irregular muffin in shape, 34·7 grams (2·5 cm diameter sphere).

KA 353 Kalgoorlie, Western Australia, from Lot 1, U.S. National Museum collection, single tektite, elongated or boatshaped, 20·8 grams (used in diffusion studies).

KA 355 Bediasite, Lee County, Texas, found resting on the Jackson formation, from Department of Geology, the Rice Institute, single tektite, rough, pock-marked sphere, 27·9 grams (2·7 cm diameter sphere).

KA 357 Kalgoorlie, Western Australia, from Lot 1, U.S. National Museum collection, 3 small tektites: muffin, 6·5 grams, button: 3·8 grams, steep-sided muffin, 3·8 grams (1 cm diameter spheres).

KA 359 Moldavite, Bohemia (?), from Department of Chemistry, Carnegie Institute of Technology, single tektite, irregular, curved leaf, translucent, yellow-green in transmitted light, 22·4 grams (1·5 cm thick plate).

KA 360 Central Sumatra, from collection at University of Utrecht, Holland, irregular weathered fragments, 8 pieces totaling 20·7 grams (0·8 cm diameter spheres).

KA 375 Empirite, Empire, Georgia, U.S.A., from U.S. National Museum, No. 1396, half of flat, ellipsoidal individual, translucent, yellow-green in transmitted light, 11·4 grams (0·6 cm thick plate).

KA 376 Tan Hai, China, approximate coordinates 110° E 21° N, from U.S. National Museum, No. 1737, 3 fragments of bubble form, concave surfaces smooth, convex surfaces rough and pitted, weights 6·2, 8·8, and 11·0 grams (0·8 cm thick plates).

KA 377 Rizalites, Philippine Islands, Pugao Babuy site, from U.S. National Museum, No. 1738, two tektites, pitted ellipsoids of revolution, weights 8·2 and 17·9 grams (2 cm diameter spheres).

REFERENCES

L. T. ALDRICH and G. W. WETHERILL (1958), Geochronology by radioactive decay, *Ann. Rev. of Nuc. Sci.* **8**, 257–298.

V. E. BARNES (1940), North American tektites, *Univ. Tex. Publ.* No. 3945, 477.

A. J. COHEN (1959), Moldavites and tektites from Georgia, U.S.A. *Geochim. Cosmochim. Acta* **17**, 150–153

C. W. COOKE (1943), Geology of coastal plain of Georgia, *U.S.G. Survey Bull.* 941.

W. D. EHMANN and T. P. KOHMAN (1958), Cosmic-ray-induced radioactivities in meteorites—II, *Geochim. Cosmochim. Acta* **14**, 364–379.

J. F. EVERNDEN, G. H. CURTIS, and R. KISTLER (1957), Potassium–argon dating of Pleistocene volcanics. QUATERNARIA, IV.

J. F. Evernden (1959), Dating of Tertiary and Pleistocene rocks by the potassium/argon method, *Proc.* Geol. Soc. London, No. 1565, 17.

W. Gentner and E. Trendelenberg (1954), Experimentelle Untersuchungen über die Diffusion von Helium in Steinsalsen und Sylvinen, *Geochim. Cosmochim. Acta* **6,** 261–267.

E. K. Gerling and M. L. Yashchenko (1952), The age of tektites, *Dokl. Akad. Nauk SSSR* **83,** 901–902.

L. M. Meredith, J. A. Van Allen, and M. G. Gottlieb (1955), Cosmic ray intensity above the atmosphere at high latitudes. *Phys. Rev.* **99,** 198.

F. J. Norton (1957), Permation of gas through solids. *J. Appl. Phys.* **28,** 34.

J. H. Reynolds (1956), High sensitivity mass spectrometer for noble gas analysis. *Rev. Sci. Instr.* **27,** 928–934.

J. H. Reynolds and G. C. Ford (1959), Absence of cosmogenic gases in a tektite, *Bull. Amer. Phys. Soc.* II, **4,** 140.

W. A. Rogers, R. S. Buritz, and D. Alpert (1954) Diffusion coefficient, solubility, and permeability for helium in glass, *J. Appl. Phys.* **25,** 868.

O. A. Schaeffer and D. E. Fisher (1959), Production of helium and neon in aluminum by 700–MeV protons and the rare gas content of stony meteorites, *Bull. Amer. Phys. Soc.* II, **4,** 140.

H. Suess, R. J. Hayden, and M. G. Inghram (1951), Age of tektites, *Nature, Lond.* **168,** 432–433.

H. S. Summers (1913) On the composition and origin of australites, Report of the Australian Assoc. for the Adv. of Sci., Melbourne Meeting, 189–199.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 115 to 121. Pergamon Press Ltd. Printed in Northern Ireland

Spectrometric measurement of natural and cosmic-ray induced radioactivity in meteorites*

M. A. Van Dilla,† J. R. Arnold‡ and E. C. Anderson†
† Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico and
‡ Institute of Technology and Engineering, University of California, La Jolla, California

(*Received* 4 *September* 1959, *revised* 8 *January* 1960)

Abstract—A nondestructive method of analysis of meteorites for natural and cosmic-ray induced radioactivity using low-level γ-ray spectrometry of kilogram samples is reported. Results so far obtained are essentially qualitative but appear to be in agreement with previous chemical measurements of K and Al^{26} in chondrites and achondrites. Cobalt^{60} was detected in the Ussuri (Sikhote-Alin) siderite (fell 1947) but not in old falls such as Odessa and Canyon Diablo. The rate of production of some interesting cosmic-ray induced activities is discussed.

Introduction

In the course of preparations for a project involving γ-ray spectroscopy of the lunar surface, we thought it would be helpful to examine the γ-ray spectra of extraterrestrial objects which have been subjected to cosmic-ray bombardment similar to that which the lunar surface receives. Since meteorites are extraterrestrial and since it has been suggested (Urey, 1959) that the chondrites may actually come from the moon, we have measured the γ-ray spectra of several meteorites with a large NaI (Tl) crystal scintillation spectrometer (Anderson and Van Dilla, 1958; Van Dilla, 1959). The crystal used was $7\frac{1}{2}$ in. in diameter by 4 in. thick. Heavy shielding minimized background, and the output pulses were fed into a 100-channel pulse–height analyser. Measurements are reported on three types of meteorites (chondrite, achondrite and siderite). The advantages of this method of measurement are:

(1) The method is completely nondestructive. The meteorite is changed in no way whatsoever, either in its physical, chemical, or radioactive properties. The sample can be measured while sealed in a plastic bag which need not be opened.

(2) Minimal handling greatly reduces the possibility of an erroneously high result because of contamination.

(3) The method is very specific. The energy of the γ-radiation is characteristic and contamination of the sample with extraneous activities (e.g. fission products) may not interfere.

(4) The method is comparatively fast (the time required for a measurement ranges from about 4 to 15 hr, depending on sample size and activity).

The disadvantages of the method, compared with other radioactivity techniques, are:

(1) The number of accessible nuclides is limited to γ-ray emitters of sufficient abundance. To date we have measured the natural radionuclide K^{40} and γ-emitting cosmic-ray activation products Al^{26} and Co^{60}. Uranium and thorium at meteoritic levels are out of reach of our present apparatus.

* Work performed under the auspices of the United States Atomic Energy Commission.

(2) Sample size must be from 0·5 to 1 kg or more.

(3) The method requires calibration to be quantitative. Since counting efficiency depends on both sample mass (self-absorption) and shape (geometrical efficiency), the calibration must be performed with a standard closely resembling the sample in these respects. For large, irregular meteorites, this is not easy. However, in the case of the determination of Al^{26} in a meteorite of known potassium content, the K^{40} peak is used an an internal standard.

Another γ-ray spectrometric method was developed independently and at about the same time by Anders (1959) for Al^{26} detection in meteorites. This

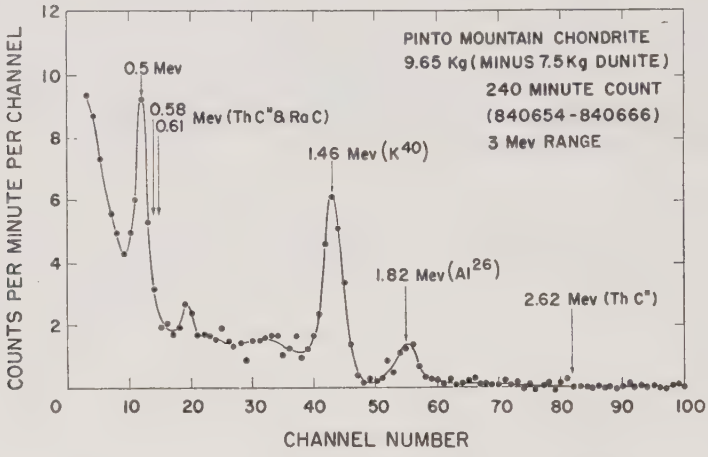


Fig. 1. γ-Ray spectrum of Pinto Mountain chondrite.

method uses a coincidence technique; results on Al^{26} in meteorites and tektites have been submitted to this journal.

The use of γ-ray spectrometry for determination of potassium, uranium and thorium in terrestrial rocks has been described by Hurley (1956) and by Adams *et al.* (1958).

Experimental Results

The accompanying graphs show the type of information obtainable by this system of measurement. The abscissae of these graphs are the numbers (from 4 to 100) of the channels into which the spectra are divided. The relationship between this scale and γ-ray energy is linear. The ordinates are the counting rates in each channel and are proportional to the γ-ray intensity. The "background" of the detector as determined with a nonradioactive* blank sample (dunite rock or steel slabs) of the appropriate size has been subtracted in all cases. The background rate varies from about 2 counts/min per 30 keV channel near 2 MeV to about 25 counts/min per 30 keV channel near 0·5 MeV.

Fig. 1 is the spectrum obtained for Pinto Mountains, a crystalline, spherulitic chondrite found in California in 1954 (La Paz, 1955). This sample was chosen for us by Dr. L. La Paz, on the basis of its recent, unweathered appearance and large

* That is, any radioactivity present is below our limit of detection.

size. Only 4 hr of counting were required for the sample; a 15 hr background measurement was used. The counting statistical errors were $\pm 0{\cdot}4$ count/min per channel at 0·5 MeV; 0·3 count/min per channel at 1·46 MeV; and 0·15 count/min per channel at 1·82 MeV, corresponding to errors of 7, 6 and 10 per cent in the peak amplitudes, respectively. As indicated on the graph, the peaks at 1·46 and 1·82 MeV are ascribable to K^{40} (half-life $1{\cdot}3 \times 10^9$ years) and Al^{26} (half-life 8×10^5 years), respectively. The peak at 0·5 MeV is uncharacteristic in that it would be produced by annihilation radiation from any positron emitter resulting from cosmic-ray activation. Its intensity relative to 1·82, however, suggests that Al^{26}

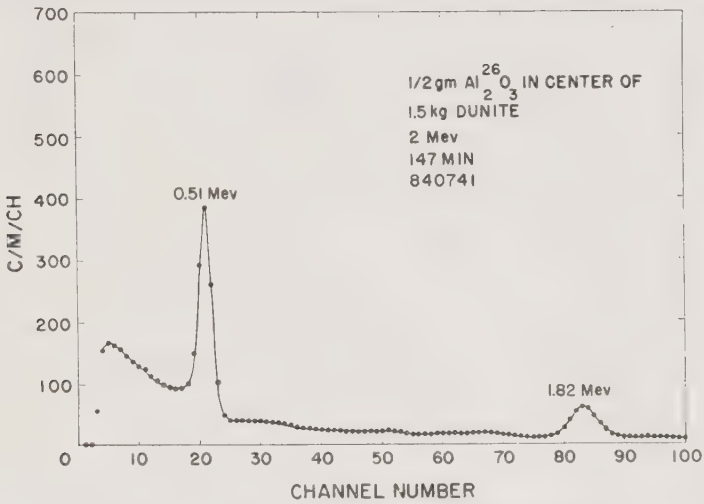


Fig. 2. γ-Ray spectrum of Al^{26} in crushed dunite.

is the principal if not the sole activity of this type. For comparison, Fig. 2 is the spectrum obtained by adding known Al^{26} activity to a sample of crushed dunite rock.

The arrows in Fig. 1 indicate the expected location of the most sensitive diagnostic lines of the thorium and uranium series. The concentration of these activities is below the limit of detection of the present system (about 20 photons/min per kg). The peak in channel 19 (0·72 MeV) is ascribable to the fission products Zr^{95}/Nb^{95} present on the surface of the specimen. This activity is widely distributed in fall-out and is the most prominent radioactivity present in ordinary dirt. Clearly, great care should be taken to protect samples from such contamination. Fortunately, the peak lies in a region of the spectrum which is of comparatively little interest at present.

The Al^{26} content of the Pinto Mountain chondrite can be calculated if the K content is assumed to be equal to the average chondritic level (0·086 per cent) reported by Edwards (1955). On this basis, the Al^{26} concentration is 65 disintegrations/min per kg. We have no standard yet for this meteorite and so have no independent K^{40} determination. In the case of Cavour, South Dakota, a brecciated, crystalline hypersthene chondrite found shortly before 1943 (weight 4·09 kgs; loaned to us by Dr. La Paz), we have been able to make an approximate mock-up;

by this means we find the K content to be 0·073 per cent and the Al^{26} content 50 disintegrations/min per kg with an experimental error of about ± 20 per cent. These values are similar to those reported by Ehmann and Kohman (1958) for Al^{26} in other chondrites and to the K values of Edwards (1955), and hence reinforce confidence in the method. Further work on standards and also on meteorites analysed by others is planned.

Fig. 3 shows the spectrum of Norton County, an olivine-enstatite achondrite (Beck and La Paz, 1951), which fell in Kansas in 1948. The principal difference from Pinto Mountain is the absence of the K^{40} peak. Norton County is reported

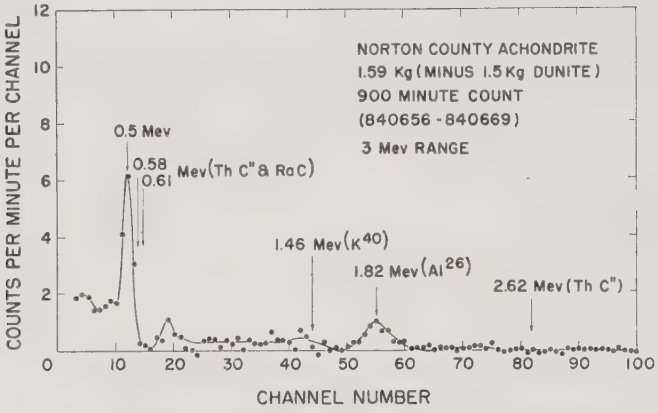


Fig. 3. γ-Ray spectrum of Norton County achondrite.

by Geiss and Hess (1958) to have a potassium content of 0·007 per cent compared with 0·086 per cent for the average chondrite (Edwards, 1955). This amount is too small to be detected in a 1·6-kg sample by our method.

Fig. 4 is the spectrum of a 1·14-kg slice of the Ussuri (Sikhote-Alin) siderite, a granular hexahedrite. In this case, both potassium and Al^{26} are below the limits of detection, and the two peaks are due to the cosmic-ray activation product Co^{60} (half-life 5·2 years). Measurements on the much older Canyon Diablo (2·0 kg) and Odessa (12·8 kg) siderites showed no detectable γ-activity of any kind. A Co^{60} activity of 10 disintegrations/min per kg would have given a significant result. The date of fall of Ussuri (12 February 1947) is long enough ago that any Fe^{59} produced extraterrestrially would have decayed away.* The possibility of Fe^{59} production by the action of cosmic radiation on iron at the surface of the earth is remote, since these spectral lines are absent from the backgrounds of large NaI (Tl) crystals in low-background enclosures at the Los Alamos Scientific Laboratory, the Hanford Atomic Products Operation, and the Argonne National Laboratory. Each of these crystals is surrounded by some 100 tons of steel shielding. The Ussuri fall is recent enough that Co^{60} produced outside the earth's atmosphere should have decayed by a factor of 5·4, whereas it would be expected to be absent

* Iron-59 has a half-life of 45 days and emits two γ-rays of almost identical energy to Co^{60}. Recent measurements of Ussuri using two large crystals gave a peak at 2·5 MeV, thus confirming the identification of Co^{60} since only in that case are both γ-rays emitted simultaneously.

in Canyon Diablo and Odessa unless supported by an Fe^{60} parent (half-life 3×10^5 years). Calibration of our equipment to permit quantitative measurements of Co^{60} is now under way; a preliminary estimate suggests the present activity in Ussuri to be roughly from 50 to 100 disintegrations/min per kg (in August 1959).

Terrestrial production of Co^{60} by capture of cosmic ray neutrons in Co^{59} seems remote. If this process accounts for the Co^{60} in the Ussuri siderite, then we would also expect cosmic ray neutrons to activate the iodine in our $7\frac{1}{2} \times 4$ in. NaI (Tl)

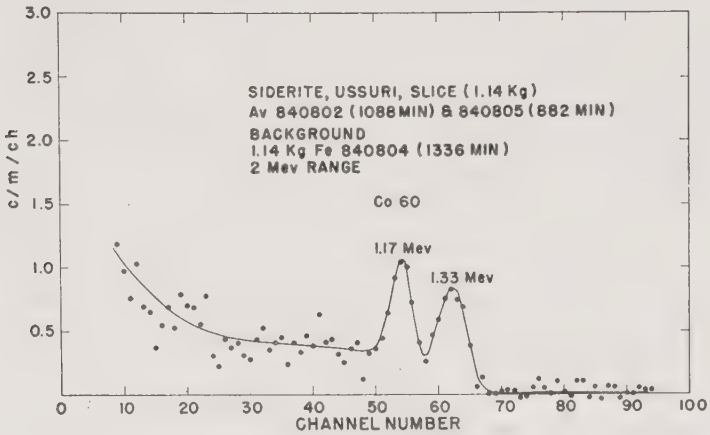


Fig. 4. γ-Ray spectrum of Ussuri siderite.

crystal, producing I^{128} (half-life 25 min, most prominent γ-ray energy 0·45 MeV, 15 per cent abundance). A neutron flux adequate to produce the Co^{60} level observed in Ussuri would give an I^{128} peak at 0·45 MeV of amplitude about 500 counts/min per 20 keV channel. We have seen no such peak in the background. Our limit of sensitivity is about 2 counts/min per 20 keV channel at 0·45 MeV, so that cosmic-ray neutrons would be expected to produce less than 0·4 Co^{60} disintegration/min per kg in a siderite. Additional evidence against terrestrial cosmic-ray activation comes from the fact that the Odessa siderite (which showed no Co^{60} activity) has been stored at the Institute of Meteoritics in Albuquerque (altitude 5000 ft) since August 1943, while the Ussuri specimen arrived there in July 1956, having been at a much lower altitude previously. Because of the strong dependence of the cosmic-ray neutron intensity on altitude (see, for example, Soberman, 1956), the Odessa should show a higher activity if terrestrial neutrons from the cosmic radiation were responsible.

Discussion

Aluminium-26 is produced in chondrites mainly by the spallation reaction $Si^{28}(p, 2pn)Al^{26}$ with contributions from $Mg^{26}(p, n)Al^{26}$ and $Al^{27}(p, pn)Al^{26}$. According to calculations to be published elsewhere, the predicted activity for Al^{26} in "small" chondrites is about 40 disintegrations/min per kg. The prediction would appear to be in rather good agreement with the data, except for the fact that it includes the assumption that the fractional production of the 6·6-second isomer

Al^{26m} (which does not decay through 8×10^5 year Al^{26}) is negligible. This fraction will have to be determined by experiment.

The situation with respect to Co^{60} in iron meteorites is much more interesting.

The production rate of Fe^{60}, the long-lived parent, by any plausible mechanism is very low. The only important high-energy reaction for Co^{60} production is $Ni^{60}(n, p)Co^{60}$, which can account for less than 10 per cent of the observed activity. The most likely mechanism is thermal neutron capture by Co^{59}.

Thermal neutron capture in meteorites has been discussed by Geiss (1957) and others in connexion with Cl^{36} production. It does not seem to have been remarked previously, however, that thermalization of neutrons in a meteorite requires a quite appreciable mass. This is especially true for irons. We estimate that even in a specimen of 1 ton original mass, most of the neutrons escape before capture. Masses of several tons are required for maximum density of thermal neutrons. Thus the dependence of the production rate of a neutron capture species like Co^{60} on meteorite mass is entirely different from that of a spallation product. This should provide a sensitive index of original meteorite mass. Excluding the small and poorly-known contribution of chlorine, the fraction of neutrons captured by each element in an average siderite are: iron, 0·79; cobalt, 0·07; and nickel, 0·14.

Since the half-life of Co^{60} is only 5·2 years, only recent falls can be measured. Nickel-59 ($\sim 8 \times 10^4$ years, electron capture, no γ-rays) is produced more abundantly than Co^{60}. The production of Co^{60} in a siderite of optimum size may be about 300 disintegrations/min per kg, while that of Ni^{59} will be about 25 per cent greater. A search for this species in irons of varying size is now underway using other techniques. As suggested by Shedlovsky (1959), Ni^{63} (half-life 125 years) will also be present in recent falls; however, its detection is still more difficult.

In stone meteorites, the thermalization process occurs in a shorter distance, and the masses given above may be divided by perhaps 10. If there is as much metal phase as is typical of chondrites, most of the neutron capture will still take place in this phase, and Co^{60} and Ni^{59} should be readily observable in suitable cases.

Acknowledgement—We are indebted to Dr. L. La Paz, Director of the Institute of Meteoritics, University of New Mexico in Albuquerque, for the loan of several meteorites (Pinto Mountains, Norton County, Ussuri, Odessa, and Cavour) used in this work, and for much valuable information and help in this general area. The Canyon Diablo siderite was purchased from Wards Natural Science Establishment, Rochester, New York.

References

Adams J. A. S., Richardson J. E., and Templeton C. C. (1958) Determinations of thorium and Uranium in sedimentary Rocks by two independent methods. *Geochim. et Cosmochim.* Acta **13,** 270–279.

Anders E. (1959) The record in the Meteorites—II. On the Presence of aluminium-26 in meteorites and tektites *Geochim. et Cosmochim. Acta* **19,** 53–62.

Anderson E. C. and Van Dilla M. A. (1958) Low-level gamma ray detection in humans. *I.R.E. Trans. Nucl. Sci.* **NS-5,** 194–198.

Beck C. W. and La Paz L. (1951) The Nortonite fall and its mineralogy. *Amer. Mineralogist* **36,** 45–59.

Edwards G. (1955) Sodium and potassium in meteorites. *Geochim. et Cosmochim.* Acta **8,** 285–294.

Ehmann W. D. and Kohman T. P. (1958) Cosmic-ray-induced radioactivities in meteorites—II. Aluminium-26, beryllium-10 and cobalt-60 in aerolites, siderites, and tektites. *Geochim. et Cosmochim. Acta* **14,** 364–379.

Geiss J. (1957) Uber die Geschichte der Meteorite aus Isotopenmessungen. *Chimia* **11,** 349–363.

Geiss J. and Hess D. C. (1958) Argon–potassium ages and the isotopic composition of argon from meteorites. *Astrophys. J.* **127,** 224–236.

Hurley P. M. (1956) Direct radiometric measurement by gamma-ray scintillation spectrometer. *Bull. Geol. Soc. Amer.* **67,** 395–412.

La Paz L. (1955) A preliminary report on the Pinto Mountains, Riverside County, California Chondrite. *Meteoritics* **1(3),** 295–299.

Shedlovsky J. (1959) Private communication.

Soberman R. K. (1956) High-altitude cosmic-ray neutron intensity variations. *Phys. Rev.* **102,** 1399–1409.

Urey H. C. (1959) *The Planets,* 2nd Ed. Yale University Press. In preparation.

Van Dilla M. A. (1959) Large crystal counting. *Nucleonics* **17(11),** 150–155.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 122 to 140. Pergamon Press Ltd. Printed in Northern Ireland

Determinations of concentrations of heavy elements in meteorites by activation analysis*

G. W. Reed, K. Kigoshi† and A. Turkevich
Argonne National Laboratory, Lemont, Illinois and Enrico Fermi Institute for Nuclear Studies, University of Chicago, Chicago, Illinois

(*Received* 20 *December* 1959)

Abstract—Barium, mercury, thallium, lead, bismuth and uranium contents and isotopic composition of stone and the troilite phase of iron meteorites have been determined by neutron activation analysis. Two groups of chondrites were observed: the one containing enstatite and carbonaceous chondrites has orders of magnitude more of the chalcophilic elements studied than other chondrites. Barium and uranium do not show this variation. The lead in this group is primordial in its 208/204 isotopic composition as might be expected from the Pb/U ratio. Some of the nuclear and geochemical implications of the results are suggested.

Introduction

Neutron activation analysis has recently been used to measure the abundance of trace heavy elements in meteorites (Reed and Turkevich, 1955; Hamaguchi *et al.*, 1957; Reed, *et al.*, 1958a; Bate *et al.*, 1957, 1958; Ebert *et al.*, 1957; Hernegger and Wänke, 1957; Reed *et al.*, 1958b). This paper reports results obtained by this method for the barium, mercury, thallium, lead, bismuth and uranium concentrations in samples of meteoritic matter. Some of the results of these analyses have already been reported (Reed *et al.*, 1958b). These early data indicated that ordinary chondrites, such as Forest City, Modoc, Holbrook, etc., which have often been used for estimating the cosmic abundances of heavy elements, are unexpectedly low in thallium, lead and bismuth. This result was confirmed by Ehmann and Huizenga (1959) who also showed that mercury was low in such meteorites.

The present paper reports more data on a larger variety of non-metallic meteorites. It has been found that samples of enstatite and carbonaceous chondrites have much larger amounts of thallium, lead and bismuth than the other types of chondrites studied. The abundances of these elements in these particular stony meteorites are closer to what might be expected on the basis of nuclear abundance regularities and current theories of nucleogenesis.

Experimental Procedures

The nuclear reactions used, the effective cross-sections, and the characteristics of the radioactive species produced, have already been presented (Reed and Turkevich, 1955; Hamaguchi *et al.*, 1957; Reed *et al.*, 1958) except for the case of mercury. In this case the radiations from the 65 hr Hg^{197} and 48 day Hg^{203} formed by (n, γ) reactions on stable mercury isotopes were measured. The large neutron capture cross-section (2300 barns) for the formation of Hg^{197} more than

* This work was supported in part by the U.S. Atomic Energy Commission.
† Present address: Gakushuin University, Mejiro, Tokyo, Japan.

compensates for the low isotopic abundance of Hg^{196} (0·15 per cent) and makes the shorter-lived activity very prominent in neutron irradiated mercury.

The meteorite samples studied, as well as their physical form and source are

Table 1. Description of meteoritic samples

Samples	Irradiation	Physical form	Source	Reference†
Forest City	6, 7 12	Powder fragments	C. C. Patterson	a, b, c, d
Modoc	6, 8, 10 13, 14	Powder fragments	H. C. Urey	a, b, c
Holbrook	8, 10 13	Powder fragments	R. R. Marshall	a, c, d
	11, 23	Fragments	H. C. Urey	
Beardsley	11	Fragments	R. R. Marshall	a, c
	19, 23	Fragments	G. Bate	
Nuevo Laredo	7, 19, 20	Powder	C. Patterson	a, b, c
Abee*	12, 14, 24	Fragments	F. Begemann	e
Indarch	14, 18			
Mighei	18	Fragments	H. C. Urey	f
Orgueil	19, 20			
Troilite from:				
Canyon Diablo	15, 16, 21	Fragments	C. Patterson	g
Toluca	16	fragments	H. Nininger	
Basalt	9	Powder	G. R. Tilton	h
Perthite	9			i

* K. R. Dawson, Geological Survey of Canada, describes Abee as a "black, polymict chondrite breccia". H. Ramberg, Department of Geology, University of Chicago, in a cursory examination was only able to identify an orthorhombic pyroxene which appeared to be enstatite.

† References to Table 1 are as follows:

(a) Hamaguchi *et al.* (1957).
(b) Patterson (1955).
(c) Bate *et al.* (1957).
(d) Marshall and Hess (1958).
(e) Begemann *et al.* (1959).
(f) Wiik (1956).
(g) Patterson *et al.* (1953).
(h) Patterson *et al.* (1955).
(i) Tilton *et al.* (1955).

listed in Table 1. In addition we have indicated some of the known previous analytical work on the same samples. As insurance against the introduction of terrestrial contamination, many samples were irradiated, without crushing, as freshly broken fragments.

The samples include four chondrites (Forest City, Modoc, Holbrook and Beardsley) that have frequently been taken as representing what we shall refer to

as "ordinary chondrites". Nuevo Laredo is an achondrite. These five meteorites have been studied previously in our laboratories (Hamaguchi *et al.*, 1957; Reed *et al.*, 1958b). Abee and Indarch are examples of enstatite chondrites; Orgueil and Mighei are carbonaceous chondrites. (See footnote to Table 1 for classification of Abee.) Two samples of troilite were studied: one from the Canyon Diablo iron meteorite and a sample from the Toluca iron meteorite. Some uncertainty exists in the identification of this latter sample as troilite. The material did not dissolve in acid. In polished sections it was revealed to be an intimate mixture of graphite and troilite. This was confirmed by chemical analysis by R. Bane of the Argonne National Laboratory.

The irradiation technique, chemical processing and counting have already been described in some detail (Reed *et al.*, 1958b). Briefly, 1–2 g samples of meteorite were sealed in quartz vials and irradiated along with monitors of meteorite powder spiked with known amounts of the elements to be measured. Most of the irradiations were carried out inside a special fuel element at the Argonne CP–5 reactor so that the fast neutrons available could be used to produce Pb^{203} from Pb^{204} by $(n, 2n)$ reactions*. This, along with Pb^{209} from neutron capture by Pb^{208}, permitted a determination of the Pb^{208}/Pb^{204} isotopic ratio as well as the lead concentration.

With few exceptions, barium, thallium, lead, bismuth and uranium were all measured in the same sample. Mercury was determined in only a few experiments; because of possible losses due to volatilization, a different procedure (see below) was used in the initial solution of the meteorite when a determination of mercury was to be made.

After the exposure to neutrons, the samples of stone meteorites were usually fused with sodium peroxide in the presence of carriers in a nickel crucible. A clear melt was considered as evidence of complete equilibration between added carriers and radioactive isotopes. When mercury was to be determined, the samples and added carriers were digested with $HClO_4$, HNO_3 and HF until only a small residue remained. In one case this residue was shown not to contain any mercury; this will be discussed later. The troilite samples were dissolved in HCl; only the residues, if any, from this acid treatment were fused.

The same radiochemical purification procedure was used for lead, bismuth, thallium, uranium and barium as described in the previous reports (Hamaguchi *et al.*, 1957; Reed *et al.*, 1958b). The mercury, when determined, was precipitated with the bismuth as the sulphide from an acid solution after the separation of the lead and barium sulphates. It was separated from the bismuth when the latter was precipitated as the oxychloride and was then brought down as sulphide. The purification cycles consisted of reduction with $SnCl_2$, precipitation of Hg_2Cl_2 with HPO_3 from dilute HCl solution, AgCl scavenging, $Al(OH)_3$ scavenging with the mercury complexed as iodide, reduction in alkaline solution with hydroxylamine sulphate, and ether extraction of the iodide complex.

As in all experiments of this type, the monitors were separated and purified in

* The effective thermal cross-section for the $Pb^{204}(n, 2n)Pb^{203}$ reaction for a sample irradiated inside an enriched uranium fuel rod is 0·002 barns and not the value given in our earlier report (Reed *et al.*, 1958b).

parallel procedures. Usually the fusion step was not performed, since complete recovery of the monitor radioactivity was possible by digestion in acid; nor was the extreme radioactive decontamination necessary.

Counting was done routinely in methane-flow proportional counters at efficiencies usually approximating 50 per cent. The very low activity samples frequently encountered were measured on a proportional counter of the same type but

Table 2. Experimental results on lead contents of meteorites

Meteorite	Expt. no.	Pb^{204} ($g/10^8$ g**)	Pb^{208} ($g/10^8$ g)	"Total Lead Content" ($g/10^6$ g†) via Pb^{204}	via Pb^{208}	Isotopic ratio§ Pb^{208}/Pb^{204}
Forest City	6*	<0·7	<0·2			
	7*	<0·64	0·09 ± 0·02		0·17 ± 0·04	
	12	0·20 ± 0·02	0·05 ± 0·01‡	0·15 ± 0·02	0·10 ± 0·02‡	
Modoc	6*	<0·2	0·05 ± 0·01		0·10 ± 0·02	
	8*	<0·14	0·02 ± 0·005		0·04 ± 0·01	
	10*	0·08 ± 0·03	<0·15	0·06 ± 0·02		
	13	0·08 ± 0·03		0·06 ± 0·02		
	14	<2·3	<0·20			
Holbrook	8*	0·55 ± 0·05	0·23 ± 0·01	0·41 ± 0·04	0·44 ± 0·02	
	10*	0·80 ± 0·20	0·19 ± 0·07	0·60 ± 0·16	0·36 ± 0·14	
	11*	0·45 ± 0·03	0·16 ± 0·01	0·34 ± 0·04	0·31 ± 0·02	
	13	0·13 ± 0·02		0·10 ± 0·02		
Beardsley	11*	0·23 ± 0·02	0·07 ± 0·01	0·17 ± 0·02	0·13 ± 0·02	
	19	<0·36	<0·15			
Nuevo Laredo	7*	0·56 ± 0·06	0·33 ± 0·03	0·42 ± 0·04	0·63 ± 0·06	59 ± 8
	20		>0·17			
Abee	12	5·6 ± 0·1	1·5 ± 0·2‡	4·20 ± 0·08	2·9 ± 0·4‡	
	14	>1·8	>0·2			
Indarch	18	3·43 ± 0·05	0·93 ± 0·03	2·56 ± 0·04	1·78 ± 0·06	26·8 ± 1·2
Mighei	18	2·34 ± 0·06	0·71 ± 0·03	1·75 ± 0·05	1·36 ± 0·06	31·1 ± 1·2
Orgueil	20	4·53 ± 0·32	1·31 ± 0·03	3·38 ± 0·25	2·50 ± 0·06	30·3 ± 1·2
Canyon Diablo troilite	15	9·2 ± 0·1	2·67 ± 0·02	6·86 ± 0·08	5·10 ± 0·04	28·8 ± 1·0
	16	10·5 ± 0·2	2·93 ± 0·03	7·84 ± 0·15	5·60 ± 0·06	27·6 ± 1·0
Toluca troilite	16	10·8 ± 0·2	3·11 ± 0·06	8·06 ± 0·15	5·94 ± 0·12	29 ± 3
Basalt	9*	9·0 ± 0·2		6·7 ± 0·2		
Perthite	9*	9·1 ± 0·2		6·8 ± 0·2		

* Experiments reported previously (REED *et al.*, 1958b), but data re-evaluated.
† The "lead content" for this column was calculated on the assumption of normal lead isotopic composition in the meteorite, even though in many of the cases the data indicate different Pb^{208}/Pb^{204} ratios.
‡ Experiment no. 12 was performed in a different part of the pile where the activation of Pb^{208} in the monitor appeared to be slightly (~20 per cent) anomalous.
§ On basis of 208/204 = 38·9 in monitor. This had been determined mass spectrometrically (REED *et al.*, 1958b).
** The units in this column ($g/10^8$ g) differ from the units in columns (4), (5) and (6) ($g/10^6$ g).

shielded with anti-coincidence counters so that its background was only 1 c/min. Thallium X-rays arising from both Pb^{203} electron capture decay and Hg^{197} β-decay were measured on a single channel scintillation counter. These data gave results in agreement with those obtained from the proportional counter measurements.

Experimental Results

Lead

Table 2 gives a summary of our experimental data on the lead contents of meteorites. Most of the results on ordinary chondrites (Forest City, Modoc, Holbrook and Beardsley) have been reported earlier (REED *et al.*, 1958b). (These

results are accompanied by symbol* in the table, and are reproduced for completeness.) In a few cases the numbers have been changed slightly as a result of reevaluation of the experimental data. The first two columns identify the meteorite and the experiment number. The third and fourth columns indicate the results for the Pb^{204} and Pb^{208} contents of the meteorite as deduced from the Pb^{203} and Pb^{209} activity, respectively. In some cases, only limits (usually upper limits) are indicated because of the possibility that the isolated radioactivity was contaminated. The fifth and sixth columns give the gross lead contents of the meteorites calculated on the assumption that the isotopic composition of the lead in the meteorites was the same as that of terrestrial lead, even though, as will be seen, this assumption is not generally valid.

Finally, in the last column, we give the Pb^{208}/Pb^{204} ratio in the meteorites from our data for those cases in which we have sufficient confidence.

The new experiments on the lead contents of ordinary chondrites confirm the earlier results, but unfortunately the activity levels are still too low to make an appreciable improvement in the data. Forest City would appear to have about 0·15 p.p.m. of lead; Modoc about 0·06 p.p.m., Holbrook about 0·40 p.p.m. and Beardsley about 0·15 p.p.m. Thus, a lead content of 0·15 p.p.m. in these chondrites appears to be a median value with a range of a factor of 3 each way.

The levels of activity in the case of these chondrites were too low in most cases to give more than an indication of the isotopic composition. In the cases where both isotopes were determined in the same irradiation, there is some indication that the lead in these meteorites may be less radiogenic than terrestrial lead.

The lead concentrations for the ordinary chondrites reported here and in our previous paper are confirmed by the mass spectrometry measurements of Marshall and Hess (1958, 1959) who observed the same range of concentrations. Their values for Forest City and Holbrook are about 0·09 and 0·3 p.p.m. (Marshall and Hess, 1958). Richardton, a chondrite, not studied here, has a lead content of about 0·1 p.p.m.

As reported earlier (Reed *et al.*, 1958), the results on Nuevo Laredo are in satisfactory agreement with Patterson (1955) in both the absolute amounts of Pb^{204} and Pb^{208} and in the very radiogenic nature of this lead ($Pb^{208}/Pb^{204} = 59 \pm 8$). Patterson (1955) reports 68 for this ratio.

The meteorites Abee, Indarch, Mighei and Orgueil stand out in having an order of magnitude more lead than the ordinary chondrites, varying between 1 and 5 p.p.m. Furthermore, the Pb^{208}/Pb^{204} ratios (27–31) are low relative to those in terrestrial lead ($\sim$39). That the lead in these meteorites should be relatively non-radiogenic is reasonable in view of their low ($\sim 10^{-8}$ g/g) uranium contents (see below). If the thorium to uranium ratios are near normal (3–4) radioactive decay in 4·5Æ could not seriously affect the isotopic composition of lead present in p.p.m. quantities. Also, these high lead results would appear to be free of suspicion from contamination since it would be hard to contaminate with primordial lead.

Finally, the lead contents of the troilite from two iron meteorites (Canyon Diablo and Toluca) are in the 5–8 p.p.m. range. This is appreciably lower than the 18 p.p.m. reported by Patterson *et al.* (1953). Our best value for the $Pb^{208}/$

Pb^{204} ratio in such material comes from the two irradiations of Canyon Diablo troilite. Fig. 1 shows the decay curve of lead from Canyon Diablo and that of a lead sample with Pb^{208}/Pb^{204} ratio of 38·9. The average of two such runs indicates a Pb^{208}/Pb^{204} ratio in Canyon Diablo of 28·2 $\pm$ 1·0. The quoted error includes an estimate of possible systematic effects; the statistical errors and agreement between the two determinations are appreciably smaller. The result is not far from the value of 29·2 reported by PATTERSON *et al.* (1953), for the lead from the troilite of this meteorite, although perhaps significantly lower. The isotopic

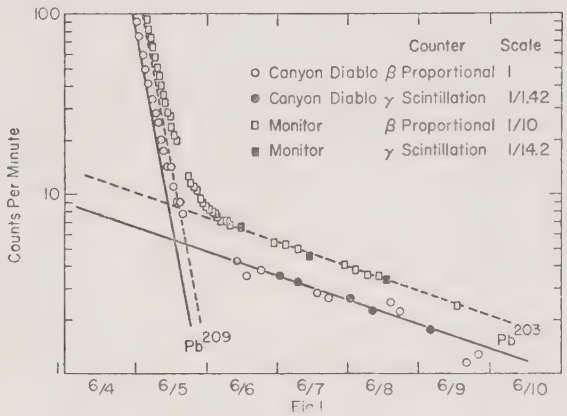


Fig. 1

Fig. 1. Decay curve of lead from Canyon Diablo troilite in comparison with that of monitor lead. The straight lines indicate the decomposition of the two components, Pb^{203} and Pb^{209}. At a time when the two species contribute equally in the case of the monitor (6/5 1400), it is seen that the sample has more Pb^{203} than Pb^{209}.

ratio (29) deduced for the troilite from the Toluca meteorite is similar to that found in Canyon Diablo. Unfortunately, in this case a slight amount of radioactive contamination prevents us from assigning an error of less than 10 per cent to the ratio.

The absolute amounts of lead found by this method in the terrestrial basalt and perthite, about 7 p.p.m. have been shown (REED *et al.*, 1958b) to be in satisfactory agreement with results obtained by PATTERSON *et al.* (1955) and TILTON *et al.* (1955), respectively, by isotope dilution methods.

Barium

Table 3 gives a summary of our experimental data on the barium contents of meteorites. These data are based primarily on the 11·6-day Ba^{131} activity induced in the samples. The correction from the β-activity of Ba^{140} from fission, was made as described by HAMAGUCHI *et al.* (1957), by La^{140} milking, and amounted to about 20 per cent in most cases.

The first column of Table 3 indicates the meteorite studied; the second gives the irradiation number; the third gives the individual results for barium contents in grammes per 10^6 g of meteorite. The probable error in these numbers is considered to be about 15 per cent except where indicated. The results on meteorites analysed previously are in excellent agreement with the values reported by

Table 3. Experimental results on the barium and "uranium" contents of meteorites

Meteorite	Irradiation no.	Barium content ($g/10^{7}$ g)	Average*	"Uranium" content ($g/10^{8}$ g)	Average†
Forest City	6	4·5	3·3	1·6	1·5
	7				
	12	2·5		1·4	
Modoc	6	4·8	3·8	1·8	1·4
	8	2·7		1·2	
	10	3·2		1·1	
	14	2·6‡		1·5	
Richardton§			3·2		
Holbrook	8	3·6	3·6	1·6	1·6
	10	3·6		2·1	
	11	3·2		1·6	
	23			1·2**	
Beardsley	11	3·8	3·0	1·7	1·2
	19	2·2		0·9	
	23			1·1**	
Nuevo Laredo	19	41·9	44	14	15
	20	44·3		17	
Abee	12	2·0	1·8	1·1	1·1
	14	1·5		1·0	
	23			1·1**	
Indarch	18	1·9		1·6	
Mighei	18	2·5		1·6	
Orgueil	19			0·8	0·8
	20	2·4		0·8	
Canyon Diablo	15	0·4		0·4	0·4
	16	<0·006		0·4	
Troilite	21	<0·3			
Toluca					
Troilite	16	<0·1		<1·3	
Basalt	9	905		84	
Perthite	9	1010		34	

* The average barium content has been calculated including the results of Hamaguchi *et al.* (1957).

† The averages listed here are from the present work only. We suspect that they are probably systematically too high by about 30 per cent (see text).

‡ An error of ~50 per cent must be assigned to the results of this measurement.

§ Richardton was not examined in this study. The results are from Hamaguchi *et al.* (1957).

** Irradiation in thermal column of Oak Ridge National Laboratory pile.

Hamaguchi *et al.* (1957). The fourth column gives the average barium content of the meteorite in question based on both present and earlier results.

The scatter of the results from individual determinations is of the order of 20 per cent in the cases of all the stone meteorites. This would appear to be real and may be a reflection of the difficulty of getting a representative sample in a 1 g sample. The average of the first five stone meteorites (ordinary chondrites) is 3·4 p.p.m. The meteorites Abee, Indarch, Mighei and Orgueil would appear to be in a slightly lower range—about 2·2 p.p.m. The present results confirm the earlier ones (Hamaguchi *et al.*, 1957) in indicating 44 p.p.m. for the barium content of Nuevo Laredo.

Information on the relative abundances of the light isotopes of barium (Ba^{130}, Ba^{132}, Ba^{134}) can be obtained from the amount of short-lived radioactivity (29–35 hr) present in the samples as compared to the 11·6-day Ba^{131} radioactivity. All of the stone meteorites examined to date show decay curves consistent with terrestrial barium isotopic ratios to within an accuracy of 5 per cent.

The barium content in the troilite phase of the two iron meteorites studied is substantially lower than that of stone meteorites. One sample of Canyon Diablo troilite gave 0·4 p.p.m.; the other two samples of troilite studied gave only limits of 0·3 and 0·06 p.p.m.

Our results for the barium concentrations in basalt (905 p.p.m.) and in perthite (1010 p.p.m.) appear to be reasonable in comparison with data in the literature on the concentration of the element in basalts and granites (Fairbairn, 1951; Engel and Engel, 1958) which give values between 500 and 2500 p.p.m. although a greater difference between basalt and perthite appears statistically to be probable.

Uranium

Table 3 also shows, in column (5), the experimental data on the uranium contents of the meteorites studied. This was calculated from the Ba^{140} contribution to the radioactivity of the isolated barium. As in our earlier work (Hamaguchi *et al.*, 1957), this contribution was determined by lanthanum "milking" of the barium after the La^{140} had grown in. The experiments thus analyse for fissionable isotopes. On the assumption that the main contribution is from the fission of U^{235} and assuming a normal isotopic ratio for the uranium—as established in our earlier work on chondrites (Hamaguchi *et al.*, 1957)—we can calculate the uranium contents from the La^{140} radioactivity.

Examination of the results listed in the table and comparison with those reported by Hamaguchi *et al.* (1957) show that the present results confirm the level of the uranium content of stone meteorites found by these authors. The scatter of the present results is a little greater, however, and the absolute amounts are somewhat higher than those reported previously. Although at present we do not completely understand the reason for this, we feel that the conditions of irradiation in most of the experiments reported here were much less suitable for a good uranium analysis than in our previous work. For example, in the present work there is some possibility of contribution from the fast fission of thorium. This is supported by the fact that irradiations of two chondrites (Holbrook and Beardsley) in the thermal flux at the Oak Ridge Pile (irradiation no.23) gave uranium

contents consistent with the lower numbers reported by Hamaguchi *et al.* (1957). Thus we feel that the uranium contents of all ordinary chondrites, including Beardsley, which had not been studied previously, are all the same—close to 1·1 $\times 10^{-8}$ g/g.

The present study, moreover, establishes that the uranium contents of Abee, Indarch, Mighei and Orgueil are just about the same as those of other stony meteorites. The approximately ten times higher value for Nuevo Laredo has been noted before (Hamaguchi *et al.*, 1957). On the other hand, the troilite from Canyon Diablo has only about one-third the uranium that typical stony meteorites have. Patterson *et al.* (1953) have reported 0·9 $\times 10^{-8}$ g/g for the uranium content of Canyon Diablo troilite—thus a little more than twice the amount we find.

The results on the terrestrial materials agree moderately well with values obtained by Tilton *et al.* (1955). He found 80 $\times 10^{-8}$ g/g and 22 $\times 10^{-8}$ g/g in the basalt and perthite as compared to our results of 84 $\times 10^{-8}$ and 34 $\times 10^{-8}$ g/g. In view of the possible contribution of thorium fission to our studies and the possible variation due to sampling at the 1 g level, this agreement must be considered satisfactory.

Bismuth

Table 4 summarizes our experimental results on bismuth. Column (3) gives the results of individual experiments on the meteorites in units of grammes of bismuth in 10^9 g of meteorite. The experiments whose results have been reported previously (in a few cases slightly re-evaluated) are indicated with a symbol.* In the case of the ordinary chondrites (the first four entries in the table) the results indicate very low and, in several cases, varying amounts of bismuth in these meteorites. In addition to the usual criteria of satisfactory decay and absorption characteristics of the β-rays, in three of the experiments the isolated radioactivity was established to be pure by further chemical purification. We therefore feel that the bismuth content of these meteorites is variable, but in all cases, very low, having a median value of 3 $\times 10^{-9}$ g/g. The meteorite Nuevo Laredo seems to be in the same class, although only limits could be established to its bismuth content.

These low values for the bismuth content of ordinary chondrites have recently been confirmed by Ehmann and Huizenga (1959), who studied several of the same meteorites using a slightly different neutron activation method. Their average bismuth content is 2·2 $\times 10^{-9}$ g/g, which is close to our median value. In addition, their results on Beardsley check our value very well. They, too, find varying results for Modoc and lower values than the average for Forest City—in this case significantly lower than the results reported here.

In marked contrast to these low figures are the bismuth contents of Abee, Mighei and Orgueil, which lie in the range 80 to 180 $\times 10^{-9}$ g/g. Indarch also has a high value in this range, although an exact number could be deduced due to radioactive contamination. Likewise, the two samples of troilite gave bismuth contents of this same magnitude (40 to 180 $\times 10^{-9}$ g/g).

Thallium

Thallium samples separated from irradiated ordinary chondrites usually

Table 4. Experimental results on the bismuth, thallium and mercury contents of meteorites

Meteorite	Irrad. no.	Bismuth content ($g/10^9$ g)	Ave. or range	Thallium content ($g/10^9$ g)	Mercury content ($g/10^9$ g)
Forest City	6*	<2·7		0·51	
	7*	1·1	1·0	0·39†	
	12	0·7		0·14†	
Modoc	6*	1·2		0·83†	
	8*	<3·4		0·14†	
	10*	0·4	0–6	0·23†	
	13	1·0		0·03†	
	14	6·2		—	
Holbrook	8*	<8	7·5	0·45†	
	10*	7·6		0·56	
	11*	1·7	2·0	3·8†	
	13	2·6		0·42†	
Beardsley	11*	3·0†	3·5	0·36†	
	19	4·1		—	
Nuevo Laredo	7*	<1		0·75	
	19	<1·6		—	0·3‡
					78·0§
					0·04**
	20	⩽1·4		0·57	
Abee	12	93		71	
	14	68	80	96†	
	24	—		—	4·0§
Indarch	14	high		—	
	18	high		125	
Mighei	18	180		97	
Orgueil	19	—		—	11,000‡
					6260§
	20	130		141	
Canyon Diablo troilite	15	40		13†	7·5§
	16	⩽65	40	7·8	5·9§
Toluca troilite	16	180		198	<34
Basalt	9*	7·6		72·5	
Perthite	9*	11		2300	

* The bismuth and thallium results of these experiments have been reported previously (Reed *et al.*, 1958b). Some of the data here have been re-evaluated.

† Sample sent through extra chemistry and found to be radiochemically pure. Almost all of the thallium samples were recycled and found to be radiochemically pure.

‡ Cold trap sample. § Acid treated sample. ** Fused residue.

contained no more than 2 c/min of activity. The long half-life of Tl^{204} made the observation of decay, which is one of the criteria for radioactive purity, impractical. As a result, chemical repurifications were carried out on most of the low activity samples. Constant specific activities (c/min per g) as well as correct absorption behaviour of the radiations were required to make the data acceptable. The spread in the data from successive purifications was in general less than 20 per cent and within the range expected from the estimated uncertainty in counting, etc.

The thallium results are compiled in column (5) of Table 4, and include our earlier reported results, in some cases slightly revised. As in the case of bismuth, the thallium contents show a tendency to scatter from sample to sample of the same meteorite. The mean thallium content of ordinary chondrites is about 4×10^{-10} g/g. This is the lowest concentration yet reported for non-volatile elements in chondrites. Nuevo Laredo, likewise, contains only about $6{\cdot}6 \times 10^{-10}$ g Tl/g. Ehmann and Huizenga (1959) find an average thallium content of ordinary meteorites (including four of those studied here) of 13×10^{-10} g/g. They also used neutron activation. Even though our levels of activity were lower, due to the shorter neutron exposure times, we feel confident of our results because of the tests of radiochemical purity which were made, and because, due to the possibility of radioactive contamination in the case of such a long-lived species as Tl^{204}, the lower results are more likely to be correct.

The carbonaceous and enstatite chondrites again have on the average 300 times more thallium than the ordinary chondrites; the concentrations range from (700–1400) $\times 10^{-10}$ g/g. Troilite has thallium concentrations in the range (100–2000) $\times 10^{-10}$ g/g.

Mercury

Analyses were conducted for mercury in stone meteorites in only the few irradiations where special control over the dissolving conditions was possible. This was because it was felt that the standard fusion dissolving procedure, geared for the short-lived Pb^{209}, might not be ideal for mercury in terms of equilibrating the radioactive mercury with the added carrier before possible vaporization losses. Moreover, in the case of two of the stones that were studied in single irradiations (Nuevo Laredo and Orgueil) an attempt was made to see if any of the radioactive mercury came off when the sample was heated to approximately 100°C for 2 hr while pumping with a mechanical pump. The pumping was done past a glass finger cooled to −78°C. Less than 1 per cent of the mercury activity was found on the cold finger in the case of Nuevo Laredo; more than 60 per cent of the activity was found in the cold trap in the case of Orgueil. Moreover, the Nuevo Laredo sample was dissolved in two stages after heating. It was first treated several times over a period of 2 days with an HF, $HClO_4$ and HNO_3 mixture, in the presence of mercury carrier. Most of the sample went into solution. The residue was fused in the presence of additional mercury carrier. This residue had less than $\frac{1}{10}$ per cent of the mercury activity of the sample. The other stone meteorites were treated only by the acid decomposition procedure.

The standard dissolving procedure in the case of the troilite samples was by

acid treatment, and here the mercury analyses were conducted in parallel with the others reported in this paper.

The mercury analyses were based on the Hg^{197} and Hg^{203} radioactivity induced in the samples. The former was often measured by both β and X-ray counting. Usually the results, calculated on the basis of the terrestrial isotopic ratios, agreed to within a few per cent.

The results of these experiments on the mercury contents of meteorites are given in column (6) of Table 4. The result of the Toluca troilite is indicated as an upper limit because in this case the X-ray counting of the induced Hg^{197} activity gave a 40 per cent lower mercury content. Likewise the results for Abee in one irradiation were so inconsistent internally as to be completely discarded. It is seen that in the only case where check experiments were performed (Canyon Diablo troilite) the agreement is satisfactory. This value for Canyon Diablo troilite, $\sim 7 \times 10^{-9}$ g/g is much lower than that of Noddack and Noddack (1931) for this meteorite (200×10^{-9} g/g).

Discussion

The analytical results reported in this paper can be examined from three relatively different standpoints. First, we can consider the results in the light of geochemical regularities observed in terrestrial rocks. This is particularly suitable in the cases of thallium and barium. Second, we can see if the results provide any new information about the nature or origin of the meteoritic samples. Finally, the nuclear implications of the data can be considered.

The geochemistry of thallium appears to be governed by the similarity of the ionic radii of K^+, Rb^+ and Tl^+ (1·33, 1·49 and 1·49 Å). Shaw (1952) has recently emphasized this point of view in a survey of the thallium contents of terrestrial rocks. These comparisons can now be extended to include meteorites. The average concentrations of thallium, rubidium and potassium in meteorites and composite terrestrial basalts and granites are given in Table 5. The meteoritic thallium data is from this paper. All the rubidium values and the terrestrial potassium values are from Gast (1959) and the meteoritic potassium data is from Edwards and Urey (1955), and Edwards (1955).

It can be seen from Table 5 that the absolute thallium concentration spreads over a much larger range (10^4) than does rubidium (350) or potassium (67) and this is reflected in the large variation in the Rb/Tl and K/Tl ratios. The meteorites show a greater variation in these ratios than do basalts and granites. It thus appears that factors other than ionic radii and charge have played a role in establishing the distribution of these three elements in meteoritic matter.

In spite of the type variations pointed out above, a very systematic trend exists in both the K/Tl ratios and Rb/Tl ratios. For each the values decrease in the following order: (1) ordinary chondrites, (2) Nuevo Laredo (basaltic achondrite), (3) basalts, (4) granites, (5) enstatite and carbonaceous chondrites. No data exists for the Rb concentration in the latter group so no check can be made of the Rb/Tl ratio.

Barium is another element for which some geochemical regularities have been noted. The range of barium contents of all stone meteorites except Nuevo Lared

is remarkably small. All the results reported here and by Hamaguchi *et al.* (1957) lie between 1·8 and 4·0 p.p.m. The ordinary chondrites are even more homogeneous, having an average value of 3·5 p.p.m. The slightly lower barium content in the carbonaceous chondrites (2·4 p.p.m.) is close to this average value if calculated on a water- and carbon-free basis. A similar relationship between some

Table 5. Potassium, rubidium, and thallium contents of meteoritic and terrestrial matter

Material	Tl	Rb*	K	K/Tl ($\times 10^3$)	Rb/Tl
	(concentrations in p.p.m.)				
Ordinary chondrites	~0·0003	2·8	850†	2800	9300
Nuevo Laredo	0·0006	0·37	470†	800	600
Orgueil	0·17		730†	4·3	
Mighei	0·11		530†	4·8	
Indarch	0·125		880†	7·0	
Abee	0·084				
Basalts (composite)	0·13	30	9600*	74	231
This work	0·073				
Granites (composite)	3·1	130	31,500*	10	42
Perthite This work	2·3				
Igneous average	1·3				

* Gast (1959).
† Edwards and Urey (1955), Edwards (1955).

carbonaceous and ordinary chondrites has been noted before in the case of their sodium and potassium contents (Edwards, 1955).

The barium contents of the two enstatite chondrites examined are lower than those of ordinary chondrites by a factor of 2. In the enstatite chondrites there is not enough volatile material to explain the deviation. The deviation of Nuevo Laredo in the opposite direction is much larger, since it has more than 10 times the barium content of the ordinary chondrites.

In terrestrial rocks, the variation in barium content has been correlated with potassium content (Engel and Engel, 1958). Our limited data suggest that in meteorites the barium follows the calcium rather than the potassium. This is illustrated by the data of Table 6. Unfortunately, the calcium content of Nuevo Laredo has not been determined; the value in the table is an average for basaltic achondrites, with which Nuevo Laredo has been grouped (Patterson, 1955).

It is, however, the variation in the abundances of thallium, lead and bismuth in the different classes of stony meteorites studied, that appears to be especially significant as regards the nature and origin of these objects. The ordinary chondrites have been shown (Reed *et al.*, 1958b) to have very low contents of bismuth and thallium, and even a relatively small amount of lead. The new results on ordinary chondrites presented here confirm these conclusions as do the recent results of Ehmann and Huizenga (1959). The latter authors also show that

Table 6. Barium, potassium, and calcium contents of meteorites

Type of meteorite	All concentrations in p.p.m.		
	Ba	K*	Ca
Enstatite chondrites	2·4	850	9000†
Ordinary and carbonaceous chondrites	3·5	880	16,000 24,000†‡
Basaltic achondrites‡			70,000
Nuevo Laredo	44	470	

* Edwards (1955).
† Wiik (1956).
‡ Urey and Craig (1953).

mercury is relatively rare in the chondrites they investigated. Our mercury content of 80×10^{-9} g/g for Nuevo Laredo is close to their average for chondrites. The other stone meteorites studied in this investigation, however (Indarch, Abee, Mighei and Orgueil) are much different in their contents of thallium, bismuth, lead and, in one case, mercury. Thallium is higher by a factor of about 200, lead by a factor of 5, bismuth by a factor of 50. The result for mercury, at least in Orgueil, is 80 times higher than the values of Ehmann and Huizenga (1959) for chondrites and our result on Nuevo Laredo. The mercury content of Abee, however, is a factor of 20 lower. In contrast with these data, the uranium and barium contents of these meteorites are very nearly the same as in all the stone meteorites (except Nuevo Laredo) examined to date.

Such a striking variation in the content of trace elements in different chondrites is very unusual. One may first try to understand it on the basis of different relative amounts of the three basic components of agglomerated meteorites, i.e. metal, sulphide and silicate. For example the amounts of thallium, lead and bismuth in the ordinary chondrites are consistent with these elements being associated with the few per cent troilite these meteorites contain, if it is assumed that this troilite is similar to that examined in this investigation. The simplest version of this picture is untenable, however, for the carbonaceous and enstatite chondrites. The sulphide content of the stone meteorites having the small thallium, lead and bismuth contents is only a factor of from 2 to 3 less than that of Indarch, Orgueil and Mighei. Moreover, these latter meteorites have amounts of Tl^{203}, Pb^{204} and Bi^{209} that are comparable to those in the separated

sulphide phase of Canyon Diablo and Toluca. Thus one cannot attribute the variation in the amounts of these elements in the stone meteorites in a simple way to the sulphide contents. On the other hand, the limited data (Nichiporuk and Chodos, 1959) indicates that perhaps the sulphide component of meteoritic matter is more variable in composition than either the silicate or metal components.

Similarly, the variation in metal content cannot be responsible. For example, Mighei and Orgueil contain no metal whereas Indarch has about 24 per cent metal; all three are similar in their thallium, lead and bismuth contents. Forest City, on the other hand, has nearly as much metal as Indarch, yet contains orders of magnitude less thallium and bismuth.

The contents of these elements is not strongly correlated with water content. It is true that meteorites containing the larger quantities of these elements contain significant amounts of water (Wiik, 1956). However, within this group the water content varies by a factor of 10 (Orgueil and Mighei cf. Indarch) without affecting the thallium, lead and bismuth concentrations.

From these remarks it seems reasonable to consider that these elements are associated with the silicate component of the meteorites. It has recently been reported that indium (Schindewolf and Wahlgren, 1960) is more than a factor of 10 lower in a typical chondrite than was expected. The chemical similarity of indium to thallium and bismuth seems significant and may be a clue to the chemical processes that appear to have removed these elements from ordinary chondrites.

The mercury content of meteorites is particularly interesting in providing information on the thermal history of these objects. Mercury and its compounds are readily lost at temperatures no greater than 350°C. Thus the variation in mercury content can be taken as an indication of thermal histories in the temperature range above that covered by the presence or absence of water.

The analytical results on mercury presented here are only fragmentary, but there appear to be three levels of mercury concentration. Nuevo Laredo, a basaltic achondrite, and the ordinary chondrites (Forest City, etc.) reported by Ehmann and Huizenga (1959) all appear to have mercury contents of about 80×10^{-9} g/g. However, the chondrite Abee, which may be typical of enstatite chondrites, falls in a class, along with the troilite phase of iron meteorites, having mercury contents in the range of $\sim 5 \times 10^{-9}$ g/g. Orgueil, a carbonaceous chondrite, contains about 6000×10^{-9} g/g. Thus, it is in the mercury concentration that a striking difference between the enstatite and carbonaceous chondrites is seen. This variation appears to be consistent with the apparent thermal history of the objects since the carbonaceous chondrites must have been at a low temperature throughout their history, having retained quite considerable amounts of water and easily decomposed organic compounds. On the other hand, polished section examination of Abee (also Indarch) reveals an almost continuous network of metal and sulphide in a silicate matrix suggesting high temperature exposure after accumulation.

We turn now to the nuclear evidence represented by these results. It has been remarked that the low abundances in ordinary chondrites of thallium, lead, bismuth and the single result on indium, if interpreted as cosmic abundances of these nuclides, are unsatisfactory in that they indicate abrupt discontinuities in elemental abundances. The results for the heavy elements in the carbonaceous

and enstatitic chondrites are much more consistent with expectations. The situation is represented in Fig. 2. The ordinate represents, on a logarithmic scale, the abundance of the odd mass nuclides, as abscissae, in the region investigated. The reference abundance is the usual one of 10^6 atoms of silicon. The dashed curve gives the abundances as deduced by SUESS and UREY (1956). The solid curve is the prediction of CAMERON (1958) from calculations based on current theories of nucleogenesis. The open and closed circles represent data obtained

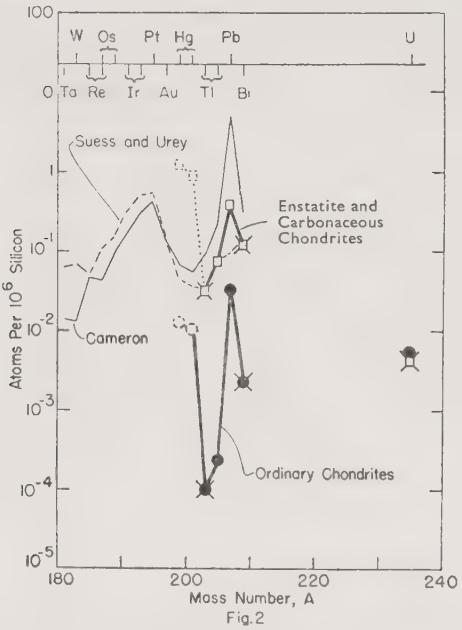


Fig. 2. Abundances of the heavy nuclei as deduced from activation analyses on meteorites in relation to abundance curves of SUESS and UREY and CAMERON.

from recent activation analysis experiments. Terrestrial isotopic composition has been assumed for mercury and thallium. The Pb^{207} point has been calculated on the basis of the Pb^{204} data and the primordial lead isotopic composition of PATTERSON *et al.* (1953). The point at mass number 235 is the abundance of U^{235} 4·5 Æ ago based on the U^{235} content today.

The experimental data on ordinary chondrites are presented as closed circles; the data for carbonaceous chondrites are shown as open squares. Except in the case of mercury, these open squares also represent the abundance curve for enstatite chondrites. The data for mercury at present is so sparse that its significance should not be overemphasized.

It is seen that the data for the ordinary chondrites in the mass region above 200 all lie far below the curves of both SUESS and UREY (1956) and CAMERON (1958). The data on carbonaceous and enstatite chondrites lie rather close to the Suess–Urey curve. They show the peak at Pb^{207} predicted by CAMERON, although the absolute amount of this nuclide is an order of magnitude less than predicted.

The agreement between the abundances of the heavy elements (except mercury)

in these special meteorites with the figures presented by Suess and Urey (1956) is most intriguing. In the case of the carbonaceous chondrites it suggests that the low-temperature history indicated by the physical character and presence of volatile compounds may have preserved a better record of elemental abundances at early times than some of the other types of meteorites previously used for this purpose.

In addition to the data on the abundance of the elements, our results also give some information on isotopic compositions. There has, of course, been considerable data reported indicating that the isotopic composition of even the heavy elements in meteorites (where not affected by radioactive decay) is the same as in terrestrial samples. For example, Hamaguchi *et al.* (1957) showed that to within 10 per cent the uranium in stone meteorites is the same as on the earth. The present data on the similarity of the Hg^{196}/Hg^{202} ratio in Nuevo Laredo, Orgueil, Abee and the troilite phase of Canyon Diablo and Toluca to that in terrestrial samples represents a check on the next heaviest element made so far.

In the case of lead, a variation in the isotopic ratio is to be expected. The age determination of meteorites and terrestrial rocks based on this variation has been widely accepted as one of the most trustworthy of such methods. A datum of great importance in this method is the isotopic composition of primordial lead. It has been assumed that the lead found in the troilite phase of iron meteorites represents such primordial lead since it has the least amount of radiogenic isotopes (Pb^{206}, Pb^{207}, Pb^{208}) relative to Pb^{204}. The present investigation confirms the findings of Patterson *et al.* (1953) in this respect, although only the Pb^{208}/Pb^{204} ratio was determined. In addition, the data shows that the enstatite and carbonaceous chondrites have Pb^{208}/Pb^{204} ratios in the same range (27–31) as the assumed primordial lead. Since the uranium (and, therefore, presumably thorium) contents of these meteorites are too low to have affected the isotopic composition of the lead, our results support the idea of a primordial lead common to many meteorites with isotopic composition close to that reported by Patterson *et al.* (1953).

Finally, the implications of these analytical results for time scales for meteoritic processes can be considered. In spite of intensive recent work, there is still only one borderline case of a meteorite in which the absolute amounts of lead, thorium and uranium are consistent, within experimental error, with an observed isotopic composition of the lead. This one case is Nuevo Laredo. Here there has been observed only 60–70 per cent of the uranium and thorium needed to produce in 4·5 Æ the amounts of radiogenic lead deduced from the isotopic composition of Patterson and our results on the absolute amount of lead present. Probably the experimental errors are sufficient to bridge this gap and so the age deduced can be trusted. In other meteorites for which Pb–Pb ages have been quoted, there is a question whether there is enough uranium and thorium to make the radiogenic lead, and the ages in our opinion must be considered suspect.

Nuevo Laredo is interesting also in giving approximate data on another time scale. Our experiments could set only an upper limit of about 2×10^{-9} g/g for the Bi^{209} content. In the same sample the U^{235} content is such that 4·5 Æ ago it was about 10^{-7} g/g. Np^{237} decays to Bi^{209} with a $2{\cdot}2 \times 10^{6}$ yr half-life. If the assumption is made that at the time the elements of this meteorite were formed,

the Np^{237} was present in amounts equal to those of U^{235} at least $1{\cdot}6 \times 10^7$ years must have elapsed between the formation of the elements and their segregation into the matter that makes up the meteorite. This lower limit is shorter than the $\geqslant 4 \times 10^8$ year deduced by similar arguments from the Xe^{129} content of meteorite (Wasserburg and Hayden, 1955; Reynolds and Lipson, 1957) but has perhaps a firmer basis since it does not depend on the retention of a noble gas.

Acknowledgements—We wish to thank Professor H. C. Urey and Drs. F. Begemann and R. Marshall for providing us with some of the meteorite samples not previously studied; Mr. R. Bane of the Argonne National Laboratory for several quantitative chemical analyses; and Dr. D. Hess of the Argonne for the mass spectrometric analysis of our lead monitor. We are indebted to Professors H. C. Urey, E. Anders, N. Sugarman, and Dr. R. Marshall for many illuminating discussions.

References

Bate, G. L., Huizenga, J. R., and Potratz, H. A. (1957) "Thorium Content of Stone Meteorites". *Science* **126,** 612.

Bate, G. L., Potratz, H. A., and Huizenga, J. R. (1958) "Thorium in Iron Meteorites". *Geochim. et Cosmochim. Acta* **14,** 118–125.

Begemann, F., Eberhardt, P., and Hess, D. C. (1959) "He^3-H^3-Strahlungalter eine Steinmeteoriten". *Z. Naturf.* **14,** 500–503.

Cameron, A. G. W. (1959) "A Revised Table of Abundances of the Elements". *Astrophysical Journal* **129,** 676–699.

Ebert, K. H., König, H., and Wänke, H. (1957) "Eine neue Methode zur Bestimmung kleinster Uranmengen und ihre Anwandung auf die Urananalyse von Steinmeteoriten". *Z. Naturf.* **12a,** 763–765.

Edwards, G. (1955) "Sodium and Potassium in Meteorites". *Geochim. et Cosmochim. Acta* **8,** 285–294.

Edwards, G., and Urey, H. C. (1955) "Determination of Alkali Metals in Meteorites by A Distillation Process". *Geochim. et Cosmochim. Acta* **7,** 154–168.

Ehmann, W. D., and Huizenga, J. R. (1959) "Bismuth, Thallium and Mercury in Stone Meteorites by Activation Analysis". *Geochim. et Cosmochim. Acta* **17,** 125–135.

Engel, A. E. G., and Engel, C. G. (1958) "Progressive Metamorphism and Granitization of the Major Paragneiss, Northwest Adirondack Mountains, New York". *Bull. Geol. Soc. Amer.* **69,** 1369–1414.

Fairbairn, H. W. (Editor) (1951) "A Cooperative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analysis of Silicate Rocks". *Bull. U.S. Geol. Survey* H980.

Gast, P. W. (1960) "Alkali Metals in Stone Meteorites". *Geochim. et Cosmochim. Acta* **19,** 1–4.

Hamaguchi, H., Reed, G. W., and Turkevich, A. (1957) "Uranium and Barium in Stone Meteorites". *Geochim. et Cosmochim. Acta* **12,** 337–347.

Hernegger, F., and Wänke, H. (1957) "Uber der Urangehalt der Steinmeteorite und deren 'Alter' ". *Z. Naturf.* **12a,** 759–762.

Marshall, R. R., and Hess, D. C. (1958) "Lead in Some Stone Meteorites". *J. Chem. Phys.* **28,** 1258–1259.

Marshall, R. R., and Hess, D. C. (1959) private communication.

Nichiporuk, W., and Chodes, A. A. (1959) "The Concentration of Vanadium, Chromium, Iron, Cobalt, Nickel, Copper, Zinc and Arsenic in the Meteoritic Iron Sulfide Nodules". *J. Geophys. Res.* **64,** 2451–2463.

Noddack, I., and Noddack, W. (1931) "Die Geochemie des Rheniums". *Z. Phys. Chem.* **154,** 223–244.

Patterson, C. C. (1955) "The Pb^{207}/Pb^{206} Ages of Some Stone Meteorites". *Geochim. et Cosmochim. Acta* **7,** 151–153.

Patterson, C. C., Brown, H., Tilton, G. R., and Inghram, M. G. (1953) "Concentration of Uranium and Thorium and the Isotopic Composition of Lead in Meteoritic Material". *Phys. Rev.* **92,** 1234–1235.

Patterson, C. C., Tilton, G. R., and Inghram, M. G. (1955) "Age of the Earth". *Science* **121,** 69–75.

Reed, G. W., Hamaguchi, H., and Turkevich, A. (1958a) "The Uranium Contents of Iron Meteorites". *Geochim. et Cosmochim. Acta* **13,** 248–255.

Reed, G. W., and Turkevich, A. (1955) "The Uranium Contents of Two Iron Meteorites". *Nature, Lond.* **176,** 794–795.

Reed, G. W., Kigoshi, K., and Turkevich, A. (1958b) "Activation Analysis for Heavy Elements in Stone Meteorites". *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva,* 1958, *Vol.* 28, *Paper* 953. United Nations, New York.

Reynolds, J. H., and Lipson, J. I. (1957) "Rare Gases in the Nuevo Laredo Stone Meteorite". *Geochim. et Cosmochim. Acta* **12,** 330–336.

Schindewolf, U., and Wahlgren, M. (1960) "The Rhodium, Silver and Indium Content of Some Chondritic Meteorites". *Geochim. et Cosmochim. Acta* **18,** 36–41.

Shaw, D. M. (1952) "The Geochemistry of Thallium". *Geochim. et Cosmochim. Acta* **2,** 118–154.

Suess, H. E., and Urey, H. C. (1956) "Abundances of the Elements". *Rev. Mod. Phys.* **28,** 53–74.

Tilton, G. R., Patterson, C. C., Brown, H., Inghram, M. G., Hayden, R. J., Hess, D. C., and Larsen, E. S. (1955) "Isotopic Composition and Distribution of Lead, Uranium and Thorium in Precambrian Granites". *Bull. Geol. Soc. Amer.* **66,** 1131–1148.

Urey, H. C., and Craig, H. (1953) "The Composition of Stony Meteorites and the Origin of the Meteorites". *Geochim. et Cosmochim. Acta* **4,** 36–82.

Wasserburg, G. J., and Hayden, R. J. (1955) "Time Interval Between Nucleogenesis and the Formation of Meteorites". *Nature, Lond.* **176,** 130–131.

Wiik, H. B. (1956) "The Chemical Composition of Some Stony Meteorites". *Geochim. et Cosmochim. Acta* **9,** 279–289.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 141 to 148. Pergamon Press Ltd. Printed in Northern Ireland

Selenium and tellurium in meteorites

Ann DuFresne
Enrico Fermi Institute, University of Chicago, Chicago, Illinois

(*Received* 4 *October* 1959)

Introduction

The concentrations of selenium in the chondritic meteorites was determined by Byers (1938) who used two observed falls and a number of finds for this purpose. He found 13 and 10 p.p.m. in Allegan and Tabory (falls), respectively, and 3 p.p.m. in Oakley (find), and did not detect the element in Tulia and Salina Township which are both finds. He also analysed a number of iron meteorites and found amounts of selenium between his limit of detection and 23 p.p.m. It is desirable that further analyses for this element be made. In addition, no reliable analyses for tellurium in chondritic meteorites have appeared in the literature.

These elements lie on rounded maxima of the Suess and Urey (1956) curves and the exact values for these abundances are needed. These authors used a somewhat higher abundance for selenium than is justified by the analytical data in order to secure smooth curves with their estimates for other elements in the same region of atomic weight. There is considerable uncertainty in regard to all abundances in the regions of selenium and tellurium as the discussion of Suess and Urey indicates. If the chondritic meteorites are an approximate sample of primitive matter, the results of this paper indicate that the abundances of these two elements are considerably lower than the values chosen for the Suess Urey tables. In view of the uncertain history of meteoritic matter, a decision in regard to this question may well be deferred for some time.

Samples

The meteorite samples were obtained from the Chicago Museum of Natural History. They were all falls, of various ages and conditions. Each sample weighed about 3 g before it was cleaned, crushed and dried. The granite used in the preliminary experiments was obtained from the Geology Department of the University of Chicago. A piece of granite weighing about 200 g was ground mechanically to provide a large stock of material of constant composition.

The meteorite samples were cleaned by chipping off the fusion crust and any other outer material which was discoloured or varnished or otherwise different in appearance from the bulk interior of the sample. The samples were then crushed in a diamond mortar and dried at 110°C before being weighed. There appeared to be no reason to suspect contamination from the paint, varnish or other impurity after this preparation, though the presence of paint or varnish is noted in the tables.

Decomposition and Separation

The samples were decomposed by fusion with sodium peroxide. Selenium and

tellurium were separated from the bulk of the material by precipitation as the metals using *gold* as a carrier.

Hydrazine hydrochloride, hydroxylamine hydrochloride, sulphur dioxide gas, saturated sulphurous acid solution, and stannous chloride were tried and found to be unsatisfactory as precipitating agents. Sodium hypophosphite was found to be a satisfactory precipitating agent. The precipitate of gold, selenium and tellurium metals was collected on a porous porcelain filter, dissolved in nitric acid, and diluted to volume. Aliquot portions were removed for the separate determinations of selenium and tellurium.

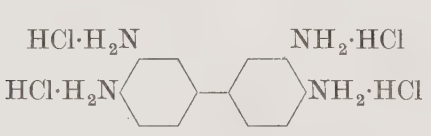
It was found that the high concentrations of gold interfered in the determination of tellurium by the iodotellurite method and that the gold was not completely removed with the selenium. A preliminary separation of most of the gold from the aliquot which was to be used for determination of tellurium was effected by an extraction with ethyl ether. The water layer was then gently evaporated to dryness and the residue was taken up in dilute HCl. Te was determined in the resulting solution.

Gold did not interfere in the determination of selenium by the diaminobenzidine method.

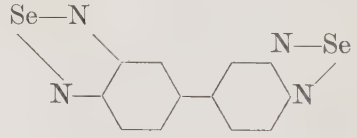
Selenium

A solution of H_2SeO_3 containing approximately 5 mg of selenium per ml was prepared. The selenium concentration of this solution was determined gravimetrically, and stock solutions were prepared by dilution of this solution. The stock solution used for testing the diaminobenzidine procedure contained 59·9 μg of selenium per ml.

The reagent used for the spectrophotometric determination of selenium (Cheng, 1956) was 3:3′ diaminobenzidine hydrochloride. In 0·1 M formic acid, one molecule of diaminobenzidine reacts with two molecules of tetravalent selenium to form the piazselenol. The structural formulae of these compounds are



3:3′ diaminobenzidine hydrochloride



piazselenol

When this project was begun, 3:3′ diaminobenzidine was not commercially available. A method for the preparation of this reagent from benzidine was found in the literature (Hoote, 1948).

Attempts to prepare the reagent by this method were made in this laboratory and also by another worker in the Chemistry Department of the University of Chicago. These attempts were uniformly unsuccessful. The several steps of the procedure were investigated. It was found that the temperature of the mixture during the nitration of the benzidine was a critical factor, and that the recommended upper limit (40°C) was too high. The temperature had to be kept well below 20°C in this step. It was found also that the removal of excess tin with H_2S was unnecessary, since the tin did not interfere in the use of the compound as a reagent for selenium.

When the commercial reagent 3:3′ diaminobenzidine hydrochloride became available from J. T. Baker and Co., Phillipsburg, Mass., it was compared with the reagent prepared in this laboratory. Separate calibration curves for the two samples of reagent were prepared by the method described below. No difference in results was observed. A single calibration curve could be drawn through all of the points. The reagent was stored as crystals in the dark. Solutions were prepared as needed and used immediately.

Table 1. Optical density measured at 420 mμ against toluene of solutions of piazselenol in toluene prepared by following the previously described analytical procedure

Solutions containing H_2SeO_3 *only*

Selenium (μg) 10 ml toluene	Optical density
0·00	0·006
12·0	0·128
23·9	0·255
35·9	0·365
47·9	0·496
47·9	0·498
59·9	0·625

Solutions containing tellurium and/or gold as well as selenium (10 *ml toluene*)

Au (mg)	Te (μg)	Se (μg)	Optical density
0	5·26	47·9	0·487
0	5·26	47·9	0·500
1·0	5·26	47·9	0·485
1·0	5·26	47·9	0·480
1·0	2·64	23·9	0·252
0	2·64	23·9	0·260
0	1·32	12·0	0·134
0	1·32	0	0·001
0	2·64	0	0·003
0	3·96	0	0·002
0	5·26	0	0·002

To prepare the calibration curve, known amounts of the stock solution of H_2SeO_3 were added to about 10 ml of concentrated HNO_3; the solution was neutralized with 7 M NH_4OH; 2 ml of 2·5 M formic acid were added and the sample diluted to 50 ml; 2 ml of 0·5% diaminobenzidine solution were added and the sample was allowed to stand for 40 min. Then the solution was brought to pH 7 with 7 M NH_4OH and an extraction was performed, using exactly 10 ml of toluene. The toluene layer was filtered and its absorption was measured at 420 mμ against a reagent blank of pure toluene. Tests showed that tellurium did not interfere. Measurements were made with a Beckman DU spectrophotometer. The calibration data are given in Table 1.

Tellurium

Several methods for the determination of tellurium were investigated. The method of Goto and Kakita (1954), a spectrophotometric method for the determination of tellurium in steel samples, was modified for use with meteorite samples. The reagent used was sodium diethyldithiocarbamate, $((C_2H_5)_2NCSSNa)$, which is reported by Goto to react with quadrivalent tellurium in 0·6 N H_2SO_4 solution to form the compound $((C_2H_5)_2NCSS)_4Te$. The latter compound may be extracted

Table 2. Optical density measured at 436 mμ against benzene of solutions of tellurium diethyldithiocarbamate in benzene prepared by following the described analytical procedure

Tellurium (μg) 5 ml benzene	Optical density
0	0·025
26·32	0·128
52·64	0·250
78·96	0·378
105·28	0·495
131·60	0·603
157·92	0·755

with benzene and the absorption measured at 436 mμ against a blank of pure benzene. It was found that results were more reproducible if the reagent, sodium diethyldithiocarbamate, was dissolved in the benzene, and the tellurium complex formed during the mixing step of the extraction process, but it was then found that this method of analysis was insufficiently sensitive for meteorite work. Table 2 gives data showing the sensitivity of the method. Larger samples could not be used because material was not available. Microextraction techniques were not studied as a means of improving the sensitivity because the Beckman DU cells and instrument must be modified for use with microlitre volume samples. Since the instrument used in this work was in use by another group at the same time, the necessary modifications could not be made. Another method of determination of tellurium was sought.

Thiourea is mentioned in the literature as a sensitive colorimetric reagent for tellurium, but preliminary experiments with rock samples to which known amounts of tellurium had been added did not yield reproducible results.

Spectrographic analysis by the copper spark method was tried. Rock samples containing known amounts of tellurium were decomposed. The tellurium was separated from the bulk of the sample and brought into solution. The solution was subjected to spectrographic examination. It was found that the method was insufficiently sensitive for the work.

Although the iodide method (Bolz, 1958) is subject to many interferences and is sensitive to small changes in experimental conditions, it was found to be usable if precautions were taken.

Tellurium tetraiodide is formed in aqueous solution which is 0·4 M in KI and 0·2 M in HCl. After 5 min the absorption of the solution was measured at 335 mμ against a water blank. A reagent blank was prepared and its absorption subtracted from each reading. Tellurium tetraiodide does not precipitate at the concentration used. Selenium (IV) interferes in this method, since it oxidizes iodide to iodine and the reaction between iodide and selenium will take place at concentrations of H^+ and I^- too low for the formation of TeI_4.

Table 3. Optical density measured at 335 mμ against water of solutions of TeI_4 in water prepared according to the described analytical procedure
(Each sample was spiked with 5 μg of Te in order to reach the reproducible concentration region for the method.)

Tellurium (μg) in 10 ml		Optical density, D
Spike	Additional Te	
5·00	0	0·250
5·00	0	0·265
5·00	0	0·260
5·00	1·00	0·295
5·00	1·00	0·310
5·00	2·00	0·332
5·00	2·00	0·350
5·00	2·00	0·333
5·00	3·00	0·380
5·00	3·00	0·360
5·00	3·00	0·400
5·00	4·00	0·415
5·00	4·00	0·412
5·00	5·00	0·449
5·00	5·00	0·440

When selenium was present, the sample aliquot was first made 0·08 M in KI and 0·05 in HCl. After 10 min a single extraction was performed, using a 1:3 mixture of amyl alcohol and ethyl acetate. The iodine was extracted and the selenium metal collected at the interface between the two phases. The organic phase was discarded. The water layer was filtered, and made 0·4 M in KI and 0·2 M in HCl. After 5 min the absorption was measured as before.

It was found that the relationship between absorption and tellurium concentration was linear and reproducible in the region from 4 to 10 μg of tellurium sample. When less than 3 μg of tellurium was present, the results were non-linear and erratic. In order to bring the samples to the level of concentration at which reproducible results could be obtained, a "spike" of 5 μg of tellurium was added to each sample. This was done in the calibration and in the determinations. Thus the "blank" sample in the calibration contained the 5 μg "spike" but no additional tellurium. This decreases the sensitivity of the method in the range of interest to us and the lower concentrations secured have a very substantial error and are probably not reliable within a factor of 2. Table 3 gives the calibration data for this method.

Details of Experimental Procedure

The finely ground sample of rock was dried for 1 hr at 110°C. From 1 to 3 g of rock was weighed into a nickel crucible. If the sample was granite, a known amount of a standardized solution of H_2SeO_3 and H_2TeO_3 was added and the sample dried again for about 15 min. If the sample was meteorite this step was omitted. From this point the treatment of granite and meteorite samples was identical.

The sample was mixed with about 8 g of sodium peroxide (Mallinckrodt AR Low Sulfur) and fused for 5 min at 600°C. The cooled melt was extracted with water and the volume of the solution was reduced to about 25 ml by evaporation. The solution was neutralized (Hydrion paper) with concentrated HCl, and then made approximately 4 M in HCl. The solution was centrifuged and the precipitate washed twice with 4 M HCl. To the clear solution was added about 1 mg of $AuCl_3$ in 200 μl of solution. Then 12–15 g of sodium hypophosphite (solid) were added to the solution in 3 g portions, with stirring after each addition. The sample was then placed on the steam bath and allowed to remain until the blue colour had disappeared and the precipitate had coagulated. The sample was filtered through a no. 3010 Selas crucible and the filtrate discarded. The crucible containing the washed precipitate was placed in a small beaker. Concentrated HNO_3 (5 ml) was poured into the crucible, and the beaker was heated on the steam bath for 30 min. The crucible was emptied into the beaker and rinsed into the beaker. The mixture in the beaker was filtered through the same crucible. The filtrate was reduced in volume if necessary, then diluted to exactly 25 ml, and 10 ml aliquot portions were taken for the separate determinations of selenium and tellurium.

Table 4. Granite samples with known amounts of selenium and tellurium added
(Decomposed and analysed by the previously described analytical procedure.)

Weight of granite (g)	Se added (μg)	Se found (μg)	Te added (μg)	Te found (μg)
2·064	0·00	0·00	0·00	0·10
2·064	0·00	0·00	0·00	0·00
1·540	4·99	4·95	0·00	0·00
1·533	4·99	4·49	2·25	1·80
1·533	4·99	4·40	2·25	2·00
2·067	9·98	9·98	4·50	4·08
2·098	9·98	9·70	4·50	4·20

For the determination of Se, the aliquot was first brought to pH 7 (Hydrion paper) with 7M NH_4OH. Two millilitres of 2·5 M formic acid were added and the solution was diluted to 50 ml. Two millilitres of 0·5% diaminobenzidine solution were added and the solution was allowed to stand for 40 min. Then the solution was brought to pH 7 with 7 M NH_4OH and an extraction was performed, using exactly 10 ml of toluene. The toluene layer was filtered and its absorption measured at 420 mμ.

To the 10 ml aliquot for determination of tellurium was added the tellurium "spike"—5 μg of tellurium in 100 μl of solution. The solution was made 8 M in HNO_3 and extracted with an equal volume of ethyl ether for removal of gold. The water layer was evaporated just to dryness on the steam bath. The residue was taken up with water, and the solution was made 0·08 M in KI, 0·05 M in HCl, and 5 ml in volume. After 10 min, the solution was extracted with 5 ml of a 1:3 mixture of amyl alcohol and ethyl acetate. After separation of the phases, the water layer was made 0·4 M in KI, 0·2 M in HCl, and 10 ml in volume. The solution was allowed to stand in the dark for five minutes and its absorption was measured at 335 mμ. Table 4 lists the results of these analyses. The determinations are generally low by about 10 per cent.

Table 5. Meteorite samples analysed by the previously described analytical procedure
(Tellurium was not determined in the finds.)

Finds Meteorite	Weight of sample (g)	Se (μg/g)
Gruver, Texas	1·695	0·96
Texline, Texas	1·592	2·50
Gladstone	1·190	2·92
Taiban	2·117	1·43

Falls Meteorite	Group	Sample weight (g)	Sulphur (%)	Se (μg/g)	Te (μg/g)	Date	Condition
Indarch	H	2·511	4·84	15·1	3·17	1891	Three pieces; paint rust on surface
Holbrook	L	3·192	2·75	13·4	1·98	1912	One piece; much crust, paint
		3·177		11·9	1·89		
Modoc	L	2·268	1·38	12·9	0·24	1905	Seven pieces; rust on surface and inside
Blanket		2·509		12·3	1·75	1909	Slice; crust, pencil marks, paint
Dhurmsala	L	2·526	2·08	10·9	1·27	1860	Many pieces; no rust
Homestead	L	2·491	2·28	10·3	0·98	1875	Large piece; no crust, no rust
Shelburne	L	3·146	1·61	9·9	2·00	1904	One piece; crust, pencil marks, varnish
Richardton	H	2·094		9·7	2·31		
Knyahinya	H	3·005	2·21	9·1	0·36	1866	Six pieces; much crust, rust
Farmington	L	3·364	1·82	8·1	1·54	1890	Two pieces; crust, no rust
Ochansk	H	3·388	1·95	7·6	1·41	1887	Pieces and powder; no rust
New Concord	L	3·481	0·12	7·3	2·12	1860	
New Concord		3·626		7·4	1·66		
Kesen		3·125	2·09	6·9	1·14	1850	Three pieces; very rusty
Bath		3·301		6·8	2·00	1892	Six pieces; much crust, much rust
Pultusk		2·591	1·07	6·3	1·38	1868	Five pieces; crust, some rust
Tilden		3·171	2·31	6·1	2·51	1937	Two pieces; no rust
Alfianello		3·072	2·71	5·8	0·23	1883	Four pieces; no crust
Queen's Mercy		3·316		5·7	0·87	1925	One piece; crust, some rust
Beaver Creek	H	3·303	1·84	5·6	0·81	1893	One piece; no crust, outside discolored
Forest City	H	3·011	2·26	5·5	1·63	1890	One piece; much crust, paint, no rust
Bjurbole	L	2·601	1·99	5·3	0·64	1899	Five pieces; no crust, some rust
			Ave.	7·90	1·34		

Analyses of Chondritic Meteorites

Twenty-two meteorites as listed in Table 5 have been analysed by these methods. The sulphur analyses have been taken from the literature using the data and references given by Urey and Craig (1953). Many of these data are unreliable as pointed out by these authors. When known, the classification into the high (H) and low (L) iron groups are given. The data have been corrected for the discrepancy between the amounts of the elements present and found as given in Table 4 by adding 10 per cent to the observed value. The probable error is about ± 10 per cent for the larger values and probably as great as a factor of 2 for the smallest tellurium data because of the necessity of adding the "spike".

Discussion of Results

It is immediately evident that the more reliable selenium data vary considerably from 13·7 p.p.m. to 4·8 p.p.m. for the observed falls and from 2·92 p.p.m. to 0·92 p.p.m. for the finds. The lower values for the finds is difficult to understand but in the absence of analytical data of the major constituents such as sulphur it is impossible to judge whether weathering may be responsible for the low values. A variation by a factor of three in the selenium abundances, and by a factor of more than 10 in the tellurium abundances for the falls show that considerable fractionation of these elements has occurred and hence we can have little confidence that the observed amounts represent the true primitive abundances. The concentrations of selenium and tellurium abundances do not follow each other nor the sulphur analyses in any regular way except that the highest amounts of all three elements occur in Indarch, which is a carbonaceous chondrite. It is evident that some fractionation process has separated these chemically similar elements. In view of such marked effects, it is not possible to regard the chondritic meteorites as reliable samples of the primitive elementary abundances of these elements and probably of other elements as well.

References

Bolz D. F. (1958) *Colorimetric Determination of Non-Metals* Vol. 8. Chemical Analysis Series, Interscience, New York.

Byers H. G. (1938) *Industr. Engng. Chem.* (News) **16,** 459.

Cheng K. L. (1956) *Analyt. Chem.* **28,** 1738.

Goto H. and Kakita Y. (1954) *Japan Analyst* **3,** No. 4, 299–304.

Hoste J. (1948) *Analyt. Chim. Acta* **2,** 402.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 149 to 153. Pergamon Press Ltd. Printed in Northern Ireland

Data of rock analyses—VII*

Bibliography and index of rock analyses in the periodical and serial literature of the Republic of Ireland and of Northern Ireland

Mary Vogt Woodland
U.S. Geological Survey, Washington 25, D.C.

(*Received* 11 *November* 1959)

The geological questions and phenomena of Ireland are far from being exhausted, and still present materials for the industrious observer.

Edward Hull, 1874

Preface

The bibliographic data of analyses of igneous and metamorphic rocks appearing in British geological literature are being published in three parts. The first part, pertaining to analyses in the Scottish literature from 1914 through 1953, has been published (Data of rock analyses: Bibliography and index of rock analyses in the periodical and serial literature of Scotland. Part VI, by Mary V. Woodland, *Geochim. et Cosmochim. Acta* 17, nos. 1–2, 136–147, 1959). This paper is the second of the three parts, and deals with the analyses published between 1914 and 1953 in the scientific journals of the Republic of Ireland and of Northern Ireland. A third part, for England and Wales, will follow at a later date. As is the case with Scotland, no analysis of a rock from an English or Welsh locality appears in the Irish literature examined; in fact, only one analysis from Scotland is recorded. Some analyses of rocks from the Republic of Ireland and Northern Ireland are first published in Scottish and in English journals; these are not included in the present paper, but will be found in parts one and three.

Part VII in this series consists of a list of the twelve periodicals and serials examined, an annotated bibliography of twenty references taken from five publications, a geographic index to the three countries represented, subdivided into counties, and a rock-name index to the forty-eight analyses contained in the references. In addition to the literature list given, several Irish archeological publications have been spot-checked for pertinent geological data, e.g. *Cork Historical and Archeological Society Journal*, *Galway Archeological and Historical Society Journal*, *County Kildare Archeological Society Journal*, *County Louth Archeological Journal*, and the *Ulster Journal of Archeology*. Only one pertinent paper was found, giving the chemical analysis of a stone axe. Dr. P. A. Sabine's assistance in this part of the literature examination is very much appreciated.

A list of previously published parts of the "Data of rock analyses" series is given on pp.86-87.

* Publication authorized by the Director, U.S. Geological Survey.

Periodical and Serial Literature

Belfast Natural History and Philosophical Society, Report and Proceedings or Proceedings and Report (1871–).
Belfast Naturalists' Field Club, Annual Report and Proceedings (1863–).
Dublin Institute for Advanced Studies, Geophysical Bulletin (1950–).
————, Geophysical Memoir (1949–).
Geological Survey of Ireland, Memoir (1904–).
————, Pamphlet (Emergency Period) (1943–1948).
Geological Survey of Northern Ireland, Memoir (1952–).
Irish Naturalist (1892–1924).
Irish Naturalists' Journal (1925–).
Royal Dublin Society, Economic Proceedings (1899–).
————, Scientific Proceedings (1877–).
Royal Irish Academy, Proceedings (1870–).

Bibliography

Dawson, J. (1951) The Brockley dolerite plug and the Church Bay volcanic vent, Rathlin Island, Co. Antrim: Irish Naturalists' Jour. **10,** no. 6, 156–162. *Northern Ireland:* 1 porcellanite.

Eyles, Victor A. (1952) The composition and origin of the Antrim laterites and bauxites: Northern Ireland Geol. Surv. Mem., 90 p. *Northern Ireland:* 5; basalt, partly kaolinized basalt, metamorphosed ferruginous bauxite, metamorphosed lithomarge, metamorphosed bauxite.

Hartley, John J. (1933) The geology of north-eastern Tyrone and the adjacent portions of County Londonderry: Roy. Irish Acad. Proc. **41,** sec. B, no. 16, 218–285. *Northern Ireland:* 1 basalt.

Hartley, John J. (1934) The white trap of Shore Road, Belfast: Irish Naturalists' Jour. **5,** no. 1, 12–15. *Northern Ireland:* 1 white trap

Holmes, Arthur (1936) A record of new analyses of Tertiary igneous rocks (Antrim and Staffa): Roy. Irish Acad. Proc. **43,** sec. B, no. 8, 89–94. *Northern Ireland:* 3; basalt, olivine dolerite, rhyolite; *Scotland:* 1 olivine basalt.

Manistre, Bernard E. (1952) The Ordovician volcanic rocks between Collon (Co. Louth) and Grangegeeth (Co. Meath): Roy. Dublin Soc., Sci. Proc. **26** (n.s.), no. 5, 113–128. *Republic of Ireland:* 3; mugearite, doleritic intrusive, autobrecciated keratophyre.

Morey, June E., and Peter A. Sabine (1953) Porcellanite axes from factories in north-east Ireland: Tievebulliagh and Rathlin—II. A petrographical review of the porcellanite axes of north-east Ireland: Ulster Jour. Archeology, ser. 3, **15,** 56–60. *Northern Ireland:* 1 porcellanite.

Patterson, Edward M. (1943) Late-stage veins in the cone-sheet of Bloody Bridge, Mourne Mountains: Irish Naturalists' Jour. **8,** no. 3, 72–76. *Northern Ireland:* 1 porphyritic hornblende granophyre.

Patterson, Edward M. (1944a) The olivine-gabbro of Ardtrea, County Tyrone: Irish Naturalists' Jour. **8,** no. 5, 171–176. *Northern Ireland:* 1 olivine zeolite gabbro.

Patterson, Edward M. (1944b) Examination of a dyke of microdiorite occurring in biotite-hornfels at Altnadua Mountain, Castlewellan, Co. Down: Irish Naturalists' Jour. **8,** no. 6, 210–214. *Northern Ireland:* 1 microdiorite.

Patterson, Edward M. (1951a) An occurrence of quartz-trachyte among the Tertiary basalt lavas of north-east Ireland: Roy. Irish Acad. Proc. **53,** sec. B, no. 14, 265–287. *Northern Ireland:* 2 quartz trachyte.

Patterson, Edward M. (1951b) Notes on three Tertiary dolerites from Counties Down and Antrim: Irish Naturalists' Jour. **10,** no. 7, 178–183. *Northern Ireland:* 1 olivine dolerite.

Patterson, Edward M. (1953) Petrochemical data for some acid intrusive rocks from the Mourne Mountains and Slieve Gullion: Roy. Irish Acad. Proc. **55,** sec. B, no. 8, 171–188. *Northern Ireland:* 4; aplitic granite, granophyre, felsite.

Reynolds, Doris L. (1942) The albite-schists of Antrim and their petrogenetic relationship to Caledonian orogenesis: Roy. Irish Acad. Proc. **48,** sec. B, no. 3, 43–66. *Northern Ireland:* 4; biotite schist, albite schist, phyllite, feldspathized phyllite.

Reynolds, Doris L. (1943) Granitisation of hornfelsed sediments in the Newry granodiorite of Goraghwood quarry, Co. Armagh: Roy. Irish Acad. Proc. **48,** sec. B, no. 11, 231–267. *Northern Ireland:* 10; cordierite biotite hornfels, trondhjemite, biotite granodiorite, porphyritic granodiorite, plagioclase biotite hornfels, granodiorite, diopside hornfels, biotite hornblende plagioclase hornfels.

Rohleder, Herbert P. T. (1932) A tectonic analysis of the Mourne granite mass, County Down: Roy. Irish Acad. Proc. **40,** sec. B, no. 12, 160–174. *Northern Ireland:* 2 basalt.

Tomkeieff, Sergei I. (1935) The dolerite plug at Ballygalley Head, Co. Antrim: Irish Naturalists' Jour. **5,** no. 10, 252–257. *Northern Ireland:* 1 olivine dolerite.

Tomkeieff, Sergei I. (1943) The Carboniferous lavas of the Ballycastle district: Irish Naturalists' Jour. **8,** no. 3, 67–72. *Northern Ireland:* 2; olivine basalt, spilite.

Tomkeieff, Serge I., and Edward M. Patterson (1947) The Tertiary igneous rocks in the neighbourhood of Ballintoy, Co. Antrim. The Knocksoghey sill: Irish Naturalists' Jour. **9,** no. 4, 89–96. *Northern Ireland:* 1 olivine dolerite.

Wager, Lawrence R. (1932) The geology of the Roundstone district, County Galway: Roy. Irish Acad. Proc. **41,** sec. B, no. 5, 46–72. *Republic of Ireland:* 2; picrite (olivine gabbro), partly altered allivalite.

Geographic Index

The localities of the igneous and metamorphic rocks for which chemical analyses are published in the Irish scientific periodical and serial literature between 1914 and 1953 are listed below alphabetically by country and by county within that country. For each country and county the appropriate author and year of publication cited in the bibliography are given, as well as the total number of analyses for that country and county.

IRELAND, REPUBLIC of 5
GALWAY 2
Wager 1932
LOUTH 1
Manistre 1952
MEATH 2
Manistre 1952
NORTHERN IRELAND 42
ANTRIM 20
Dawson 1951
Eyles 1952
Hartley 1934
Holmes 1936
Morey and Sabine 1953
Patterson 1951a
Reynolds 1942
Tomkeieff 1934, 1943
Tomkeieff and Patterson 1947
ARMAGH 14
Patterson 1951a, 1953
Reynolds 1943
DOWN 6
Patterson 1943, 1944b, 1951b, 1953
Rohleder 1932

TYRONE 2
Hartley 1933
Patterson 1944a
SCOTLAND 1
ARGYLL 1
Holmes 1936

Rock Name Index

Allivalite, partly altered	Wager 1932
Basalt	Eyles 1952; Hartley 1933; Holmes 1936; Rohleder 1932
olivine	Holmes 1936; Tomkeieff 1943
partly kaolinized	Eyles 1952
Dolerite, olivine	Holmes 1936; Patterson 1951b; Tomkeieff 1935; Tomkeieff and Patterson 1947
Doleritic intrusive	Manistre 1952
Felsite	Patterson 1953
Gabbro	
olivine	Wager 1932
olivine zeolite	Patterson 1944a
Granite, aplitic	Patterson 1953
Granodiorite	Reynolds 1943
biotite	Reynolds 1943
porphyritic	Reynolds 1943
Granophyre	Patterson 1953
porphyritic hornblende	Patterson 1943
Hornfels	
biotite hornblende plagioclase	Reynolds 1943
cordierite biotite	Reynolds 1943
diopside	Reynolds 1943
plagioclase biotite	Reynolds 1943
Keratophyre, autobrecciated	Manistre 1952
Metamorphosed bauxite	Eyles 1952
Metamorphosed ferruginous bauxite	Eyles 1952
Metamorphosed lithomarge	Eyles 1952
Microdiorite	Patterson 1944b
Mugearite	Manistre 1952
Phyllite	Reynolds 1942
feldspathized	Reynolds 1942
Picrite	Wager 1932
Porcellanite	Dawson 1951; Morey and Sabine 1953
Rhyolite	Holmes 1936
Schist	
albite	Reynolds 1942
biotite	Reynolds 1942
Spilite	Tomkeieff 1943
Trachyte, quartz	Patterson 1951a
Trap, white	Hartley 1934
Trondhjemite	Reynolds 1943
White Trop	Hartley 1934

List of Published Parts of the Series

Marjorie Hooker (1956) Data of rock analyses, Part I. African periodical and serial literature *Geochim. et Cosmochim. Acta* **9**, nos. 1–2, 90–97.

Marjorie Hooker (1956) Data of rock analyses, Part II. Bibliography and index of rock analyses in the African periodical and serial literature. *Geochim. et Cosmochim. Acta* **9,** no. 4, 190–213; Suppl., **11,** nos. 1–2, 138.

Marjorie Hooker (1957) Data of rock analyses, Part III. New Zealand periodical and serial literature. Bibliography and index of rock analyses. *Geochim. et Cosmochim. Acta* **11,** nos. 1–2, 130–138.

Marjorie Hooker (1958) Data of rock analyses, Part IV. Icelandic periodical and serial literature. Bibliography of rock analyses. *Geochim. et Cosmochim. Acta* **15,** nos. 1–2, 30–31.

Marjorie Hooker (1959) Data of rock analyses, Part V. Bibliography and index of rock analyses in the Australian periodical and serial literature. *Geochim. et Cosmochim. Acta* **15,** no. 4, 342–369.

Mary V. Woodland (1959) Data of rock analyses, Part VI. Periodical and serial literature of Scotland. Bibliography and index of rock analyses. *Geochim. et Cosmochim. Acta* **17,** nos. 1–2, 136–147.

Geochimica et Cosmochimica Acta, 1960, Vol. 20, pp. 154 to 160. Pergamon Press Ltd. Printed in Northern Ireland

GEOCHEMICAL NOTES

Beryllium in Tanganyika granitic rocks

(*Received* 14 *March* 1960)

In the course of the investigation of a number of the properties of granites and granodiorites of Tanganyika, 284 specimens were analysed for beryllium. Of these, forty-two were found to contain more than the detection limit of the method (which was between $\frac{1}{2}$ and 1 p.p.m. Be). Two were found to contain more than 5 p.p.m. Be and none more than 10 p.p.m.

The specimens were taken from the collections of a number of past and present officers of the Department of Geological Survey and may be assumed to include representative material from all the recognised types of granites and granodiorites in the territory (Harpum, 1960). The investigation has touched upon seventeen of the twenty-two major occurrences of granitic material in Tanganyika. The exceptions are those located in the Songea, Musoma, Kahama-Shinyanga, Singida and Ukimbu areas.

A spectrographic method of analysis was used which had a moderate precision (about ±30 per cent) for the higher values but possibly poorer precision as the limit of detection was approached. The accuracy of the technique, as deduced from linearity of working curves based upon synthetic standards (which were prepared by a number of methods), was estimated to be of the same order as the precision.

The figures summarized in the Table 1 are generally lower than those used by Sandell (1952) in his calculation of the average beryllium content of granitic rocks and nearer to

Table 1. Beryllium in Tanganyika granites and granodiorites

Rock type	Locality	Age	Number of specimens	No. containing detectable Be*
Synorogenic granodiorite	Ugogo	Early Archean	36	1
	Geita		12	0
	Nzega		1	1
Synorogenic granite	Ugogo		24	4
	Geita		3	3
	Biharamulo		2	1
Synorogenic granodiorite	Nachingwea	Late Archean	14	0
	Ubena		10	0
	Magubika		2	0
Synorogenic granite	Nachingwea		12	1
	Ubena		11	0
	Sao Hill	?	1	1
	Kondoa	?	2	0
Late-orogenic granite	Nzega	Early Archean	1	1
	Geita		4	2
Late-orogenic granodiorite	Msusule	Late Archean	15	1
	Lupa		25	0
Late-orogenic granite	Karagwe	Early Proterozoic	31	9
Post-orogenic granodiorite	Njombe Dist.		6	2
Post-orogenic granite	Njombe Dist.		28	1
	Kate		19	12
Aplites and pegmatites in synorogenic granitic rocks	Geita	Early Archean	4	0
		Total	284	42

* Detection limit between $\frac{1}{2}$ and 1 p.p.m. Be.

the figures of NORTON *et al.* (1958). Check analyses on four selected specimens carried out by the National Chemical Laboratories, Teddington, Middlesex, served only to confirm that the beryllium content of the submitted samples did not exceed 10 p.p.m.

On the basis of HARPUM's geological division of the specimens which have been examined, the following trends suggest themselves. In some cases the data are not sufficiently numerous to warrant true statistical analysis.

(a) Beryllium would appear to be more frequently found in granites than in granodiorites (23 per cent of granites show detectable Be and only 4 per cent of granodiorites).

(b) Beryllium is most frequently found in late-orogenic granites, less frequently in post-orogenic granites and least frequently in synorogenic granites (33 per cent of late-orogenic granites, 22 per cent of post-orogenic granites and 18 per cent of synorogenic granites contain detectable beryllium).

(c) The incidence of detectable beryllium is most marked in Early Archean granites (32%), less so in Early Proterozoic granites (24%) and least marked in Late Archean granites (8%).

These latter two observations refer to the granites and not the granodiorites.

I wish to thank my colleagues in this Department for their co-operation in this work, the Officer-in-charge UKAEA, Dodoma for arranging the check analysis at NCL, Teddington and the Director of Geological Survey for permission to publish these results.

Dept. of Geological Survey, Dodoma, Tanganyika

B. J. RUSHTON

REFERENCES

HARPUM J. R. (1960) Granitic and metamorphic associations in Tanganyika. *Proceedings of the International Geological Congress, Copenhagen.* In the press.

NORTON J. J. GRIFFITTS W. R. and WILMARTH V. R. (1958). Geology and resources of Beryllium in the United States. *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva,* 1958. United Nations, New York.

SANDELL E. B. (1952) The beryllium content of igneous rocks. *Geochim. et Cosmochim. Acta* **2,** 211–216.

Cohenite as a pressure indicator in iron meteorites

(*Received* 3 *March* 1960)

COHENITE $(FeNi)_3C$ has been recorded in the following meteoritic irons, Magura, Bendego, Wichita County, Beaconsfield, Canon Diablo, Pittsburgh, Crosby Creek, Breece and Youndegin. PERRY (1944) points out that this mineral is probably more widespread than these occurrences would suggest since it is very difficult to distinguish from schreibersite.

Cohenite is similar to cementite (Fe_3C) which occurs in steels. It differs in containing up to 3 per cent nickel in solid solution (FARRINGTON, 1915). A large amount of data are available on the properties and behaviour of cementite. Thermodynamic and experimental studies have shown that it is unstable relative to carbon saturated iron and graphite throughout the whole temperature range below the eutectic at 1153°C (WELLS, 1938; DARKEN and GURRY, 1951). In steels, cementite mostly forms in the region between 1150°C and 730°C (approx.). In this region its metastability is not very pronounced, the free energy change for reaction (1):

$$\underset{\substack{\text{(Iron saturated}\\ \text{with carbon)}}}{3Fe} + \underset{\text{graphite}}{C} \rightarrow \underset{\text{cementite}}{Fe_3C} \qquad (1)$$

at 1000°C being only about +60 cal. However, the free energy change of this reaction increases very rapidly (positively) as the temperature falls below 700°C DARKEN and GURRY, 1951; Table 1), reaching 4800 cal at 25°C. Thus, in steels, cementite is formed as a slightly metastable phase. As the steel is cooled, or quenched, the metastability increases, but diffusion and nucleation rates are rapidly decreased, so that cementite is preserved at room temperature.

Table 1. Pressures required for stability of cementite according to reaction (1)

Temperature (°C)	Free energy of formation* $F°$ (cal)	Pressure p(bars)
300	3100	38,100
400	2350	28,900
450	2000	24,600
500	1650	20,300
600	1000	12,300
700	400	4,900

* $\Delta F°$ values are from DARKEN and GURRY, (1951).

When cementite-carrying steels are annealed for long periods at high temperature, equilibrium is reached and the cementite is observed to break down to graphite and iron. Thus WELLS (1938) observed partial breakdown of cementite in pure Fe–C alloys which had been subjected to a temperature of 925°C for 20 hr. Partial breakdown was also observed in alloys subjected to 700°C for 150 hr. WELLS observed that the rate of graphitization was largely influenced by nucleus formation. If a steel was held at high temperature for a time sufficient to form graphite nuclei and then annealed for longer times at lower temperatures, complete graphitization of cementite was observed. This occurred in an alloy subjected to 1050°C for 72 hr, 950°C for 24 hr, 850°C for 24 hr, 750°C for 48 hr, and 675°C for 96 hr.

The kinetics of graphitization in an automobile steel were studied by SCHWARTZ and BARRETT (1938). They found approximately equivalent graphitization (about 0·2) in a steel which had been subjected to the following treatments.

600°C	700°C	800°C	900°C
260 hr	73 hr	14 hr	1·6 hr

Logarithmic extrapolation of the data indicated that a similar degree of graphitization would be reached in 1100 hr at 500°C, 4500 hr at 400°C, and 20,000 hr at 300°C.

The rate of graphitization is affected by the presence of other elements. In particular, nickel is observed to accelerate the decomposition of carbide. This is due to the fact that Ni_3C is much more unstable than Fe_3C. At 250°C, the free energy (ΔF) of formation of Ni_3C is −8900 cal compared to +4760 for Fe_3C. In the higher temperature region, above 700°C, where carbides are precipitated, the relative differences are much greater. ΔF for Ni_3C is around +2000 cal whereas ΔF for Fe_3C decreases to a minimum of +54 cal. The higher rate of graphitization in SCHWARTZ and BARRETT'S experiments compared to those of WELLS, is probably due to the fact that the former workers used nickel-containing steel, whereas the latter used pure iron. The graphitizing action of nickel is most important when these results are extended to meteorites.

Iron meteorites have cooled from a molten state very slowly. Occurrence of continuous

Widmanstätten textures over distances of 10 ft show that the parent taenite crystals must have been at least this large. This indicates slow cooling through the higher temperature region. Uhlig (1954) points out that the coarseness of Widmanstätten textures implies very slow cooling through the γ–α transition region. Uhlig (1954) and Urey (1956, 1958) have made estimates of the times required to form Widmanstätten textures. These differ since the authors disagree on the final temperature at which equilibrium was reached. Estimates range from 450°C to 300°C. The corresponding times required are between 10^7 and 10^{11} years.

The enormous annealing periods which iron meteorites have received are many orders of magnitude longer than would be required to completely decompose cementite or cohenite. It should also be noted that meteoritic irons have cooled very slowly through the 1000°C–700°C region in which graphite nuclei are readily and quickly formed. Subsequent slow cooling to much lower temperatures in the presence of graphite nuclei decreases many hundredfold the times required for cohenite decomposition at these temperatures (Wells, 1938). Finally the presence of about 8 per cent nickel in meteoritic irons in which cohenite is found would also considerably accelerate the graphitization.

The retention of cohenite in meteoritic irons therefore implies that some factor which does not enter into the time–temperature–decomposition experiments cited above has contributed to cohenite stability in meteorites. The occurrence of cohenite in rounded crystals up to 8 mm long in meteorites, compared to the minute crystals or pearlitic intergrowths found in steels also suggests that it has crystallized as a thermodynamically stable phase.

The molar volumes of iron, graphite and cementite are 7·11 cm^3, 5·30 cm^3 (Berman and Simon, 1955) and 23·23 cm^3 (Lipson and Petch, 1940). Thus reaction (1) proceeds towards cementite with a diminution in volume of 3·40 ml. The formation and stability of cohenite in meteorites is therefore strongly favoured by pressure. By far the most likely explanation for the occurrence of cohenite in meteorites is that they have crystallized under pressures sufficiently high to make cohenite thermodynamically stable.

To a first approximation, the contribution by pressure to the free energy change of reaction (1) is given by $P.\Delta v$, where P is the pressure and $\Delta v = 3{\cdot}40$ cm^3. When this quantity is equal to ΔF°, the free energy for reaction (1) at zero pressure, equilibrium is reached. The relevant calculations have been made and the results are set out in Table 1.

These pressures would be increased if allowance had been made for the effect of compressibility on Δv, which is decreased at high pressure, owing to the relatively high compressibility of graphite. The calculated pressures would also have been increased if allowance was made for the effect of nickel in solid solution in cohenite.

Uhlig (1954), Henderson and Perry (1954) and Urey (1958) agree that meteoritic irons cooled very slowly to a temperature of 450°C or below. Thus all meteorites containing cohenite must have cooled under pressures exceeding 25,000 atm (Table 1) to that temperature. This indicates that meteoritic irons crystallized deep within a parent body approximately of lunar size. Urey (1956) reached a similar conclusion based upon the occurrence of diamond in irons.

A. E. Ringwood

Australian National University, Canberra

References

Berman R. and Simon F. (1955) *Z. Electrochem.* **59,** 333.

Darken R. S. and Gurry R. W. (1951) *J. Metals* **3,** 1015

Farrington O. C. (1915) *Meteorites* p. 156. Lakeside Press, Chicago.

Henderson E. P. and Perry S. H. (1954) A discussion of the densities of iron meteorites, *Geochim. et Cosmochim. Acta* **6,** 221.–240

Lipson H. and Petch N. J. (1940) *J. Iron and Steel Inst.* **142,** 95.
Perry S. H. (1944) Metallography of Meteoritic Iron. *U. S. Nat. Mus. Bull.* **184,** 21.
Schwartz H. A. and Barrett M. K. (1938) *Trans Amer. Soc. Metals* **26,** 358.
Uhlig H. H. (1954) Contribution of metallurgy to the origin of meteorites—I. *Geochim. et Cosmochim. Acta* **6,** 282–301.
Urey H. C. (1956) *Astrophys. J.* **124,** 623.
Urey H. C. (1958) *Proc. Chem. Soc.* 67.
Wells C. (1938) *Trans. Amer. Soc. Metals* **26,** 289.

The relationship between the fractionation stage of basalt magma and the temperature of the beginning of its crystallization

(*Received* 26 *May* 1960)

Crystal fractionation of basic magma, in the early and middle stages, is dominantly controlled by the separation of olivine, basic plagioclase and pyroxenes. Because the early, high-temperature ferromagnesian minerals of a solid solution series are richer in magnesium than the later, lower-temperature members, there is an increasing proportion of iron relative to magnesium in the successive crystal fractions and in the corresponding residual liquids. Similarly, because the early high temperature plagioclases are richer in anorthite, there is an increasing proportion of albite relative to anorthite in the successive crystal and liquid fractions. These generalizations are satisfactorily based on observations of naturally occurring cases of fractionation of basic magma, and on experimental investigations of systems involving olivine, plagioclase or pyroxene. Although there is a difference of opinion about the extent of total iron enrichment during fractionation, there is none about the increase in iron relative to magnesium, nor about the increase of albite relative to anorthite. Thus for ordinary basic magma from which olivine, plagioclase and pyroxene separate, two chemical factors, the iron ratio $\left(\frac{Fe^{2+} + Mn}{Mg + Fe^{2+} + Mn}\right)$ and the albite ratio $\frac{\text{Normative Ab}}{\text{Normative Ab} + \text{An}}$ are recognised as providing an indication of the extent of fractionation. If these two parameters are plotted against each other the spread of points may be divided into arbitrary stages as was done in a recent paper on fractionation stages of basic lavas (Wager, 1956).

Generally speaking, basalts of an early stage in the fractionation process should be those with low albite and iron ratios, while basalts of successively later stages of fractionation should have increasingly higher values. It was pointed out in the paper referred to that "the basalt materials of the different stages will differ in the temperature required to make them completely liquid, the early-stage basalts being the higher temperature, and the late-stage, the lower". (*op. cit.* 1956, foootnote p. 223; see also p. 219). In the same place it is also stated that "it would have been, in many ways, more satisfactory to have used the terms high-, middle-, and low-temperature basalts" in place of early, middle and late stage basalts, but this terminology was avoided as not being a direct deduction from observation.

Highly interesting experimental results on the range of melting temperatures of basalts of various magma types are given by Yoder and Tilley in the Annual Report of the Carnegie Institution (1957, pp. 156–61). Although only five basalts have been so far investigated in this way, it is of interest to compare the results with the fractionation stage of the basalts deduced from their chemical composition.

The five basalts dealt with by Yoder and Tilley are named in Fig. 1 which is taken from their paper with an additional right hand column. The analyses of these basalts (Yoder and Tilley, *op. cit* p. 157 and Macdonald, 1949, p. 63 No. 11) together with all analysed Hebridean

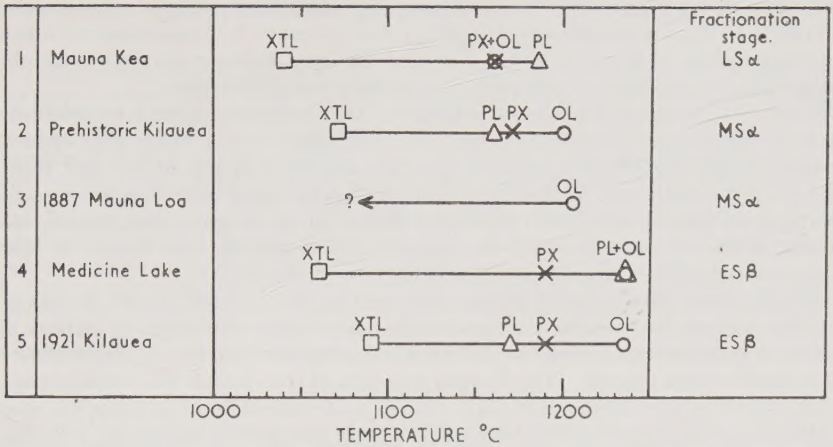


Fig. 1. Results of thermal treatment of selected basalts after YODER and TILLEY, with the basaltic fractionation stages deduced from the analyses. The temperatures at which plagioclase, olivine and pyroxene appear on crystallization of the melt are shown, and the temperatures when completely crystallized (XTL).

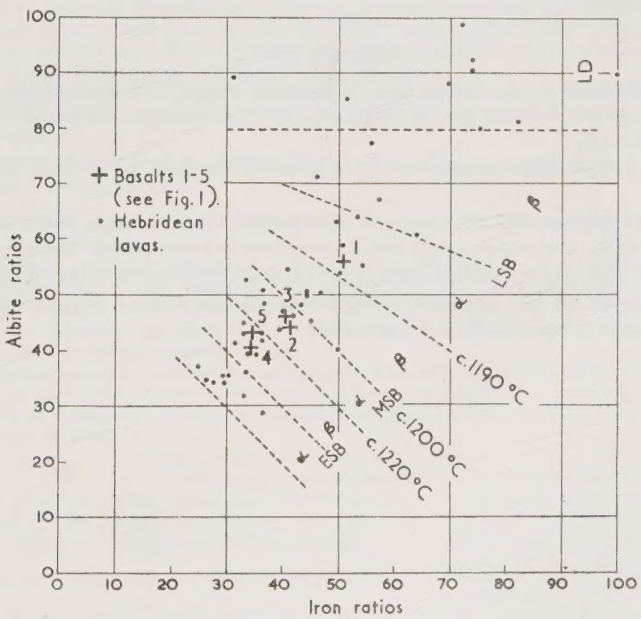


Fig. 2. Albite and iron ratio plot of the five basalts investigated by YODER and TILLEY divided into fractionation stages together with plots of all analysed Hebridean lavas for comparison. The approximate temperatures of certain of the boundaries of the fractionation stages are also shown.

lavas for comparison, are plotted on an albite and iron ratio plot in Fig. 2, where the division into fractionation stages is also shown. Basalts 4 and 5 belong to the ES_β stage, basalts 2 and 3 to MS_α and basalt 1 to $LS\alpha$. The temperatures found experimentally by YODER and TILLEY to be necessary to liquefy these basalts completely are given in Fig. 1, together with the sequence of phases separating on cooling. The order of the temperatures required to produce complete melting is the same as the order of the fractionation stages deduced from the analyses. So far as

the present data go, it appears that basalt of the ES_β fractionation stage requires a temperature of about 1230°C to melt it completely, the MS_α basalt requires a temperature of about 1210°C, and LS_α a temperature of about 1180°C. Three of the lines defining the fractionation stages of Fig. 1 are assigned approximate temperatures on the basis of this data.

Yoder and Tilley point out that the range of temperature required to produce complete liquefaction of these diverse basalts is small. Nevertheless it seems likely that even such small differences are highly significant and that they are reflected in the Albite and Iron ratios as determined from the analyses. In the fractional crystallization of the Skaergaard magma, 80 per cent of the magma was crystallized to produce a change in the magma from the ES_β stage to the MS_α (Wager, 1960). On the basis of the limited data available, this degree of fractionation apparently occurred over a range of temperature of only about 50°C.

Although the term fractionation stages was used in the original paper, it was noted that basalts of the various fractionation stages might have been produced by partial melting of certain types of pre-existing material at different temperatures (*op. cit.*, p. 223) rather than by a fractional crystallization process. The Karroo dolerites of the earliest fractionation stage are on the boundary between the primary and early stages, while the earliest fractionation stage basalts from the Deccan are on the boundary between the early and middle stages (*op. cit.*, Figs. 8A and B). If produced by partial melting the earliest Karroo dolerite magma would have a considerably higher temperature of formation than the earliest Deccan lavas.

L. R. Wager

Department of Geology and Mineralogy
The University Museum,
Oxford

References

Yoder H. S. and Tilley, C. E. (1957) Basalt Magmas. Annual Report of the Director of the Geophysical Laboratory, Carnegie Institution of Washington. *Carnegie Inst. Washington Year Book* **56**, 156–161.

Macdonald G. A. (1949) Petrography of the island of Hawaii. *U.S. Geol. Surv. Prof. Paper* 214-D, 51–96.

Wager L. R. (1956) A chemical definition of fractionation stages as a basis for comparison of Hawaiian, Hebridean, and other basic lavas. *Geochim. et Cosmochim. Acta* **9**, 217–248.

Wager L. R. (1960) The major element variation of the layered series of the Skaergaard intrusion and a re-examination of the average composition of the hidden layered series and of the successive residual magmas. *J. Petrol.* (in press)

INFORMATION FOR CONTRIBUTORS

I. GENERAL

1. Papers on *geochemistry* should be submitted to the appropriate Executive Editor—Prof. L. R. WAGER for papers from the United Kingdom and British Commonwealth, and for papers in English from Europe; Prof. C. W. CORRENS for papers in German or French; Prof. E. INGERSON for papers from the American continents. Papers on *cosmochemistry* should be sent to Prof. W. A. WAHL. Papers submitted for publication will naturally be judged from the standpoint of scientific originality and novelty. Technical details of apparatus used in scientific investigation can, however, be presented in brief notes. Critical comments or preliminary results requiring early publication should be submitted as letters to the editors. Where possible, letters should be confined to 500 words. The preparation of progress reports and review articles will be invited by the editors from time to time. The journal appears as independent and complete numbers, which are combined into volumes of about 300 pages.

2. Only papers which have not been previously published can be accepted. Authors must agree not to publish elsewhere a paper submitted to and accepted by *Geochimica et Cosmochimica Acta*.

3. Fifty reprints of each paper are provided free. Additional copies can be purchased if ordered at the time the first proofs are returned. A reprint order form will accompany first proofs.

II. SCRIPT REQUIREMENTS

1. Scripts must be written in one of the three official languages—English, French or German.

2. The script should be typed (not a carbon copy). The text must be ready for printing and should be carefully checked for errors. Authors will receive proofs for correction.

3. Illustrations should accompany the script, mounted on separate sheets. Line diagrams that require to be redrawn should include all relevant details. Half-tone illustrations should be restricted to the minimum necessary. Photographs should be enlarged sufficiently to permit their clear reproduction and if words or numbers appear on them, two copies should be sent, one clearly printed and the other without inscription. All illustrations should be provided with descriptive legends, which should be given on a separate sheet. Any lettering on diagrams—other than Greek letters, symbols, etc.—should be stencilled and should be sufficiently large and bold to permit reproduction when the diagram has been reduced to a size suitable for inclusion in the journal.

4. References in the text should be given by quoting the author's name and year of publication, i.e. AHRENS (1952). *Full references should be listed at the end of each paper, in alphabetical order, in the following manner*

AHRENS, L. H. (1952). The use of ionization potentials—I. Ionic radii of the elements. *Geochim. et Cosmochim. Acta* **2**, 155–169.

and should include the full title of the article, standard abbreviated title of the journal, year, volume number and inclusive page numbers.

5. The text of articles submitted should be concise and in a readily understandable style. The technical description of the methods used should only be given in detail when such methods are new. The essential contents of each paper should be briefly recapitulated in an abstract in English. Such an abstract, may, however, be submitted by the author in the language of the original typescript for translation into English by the editorial staff.

6. To conserve space, authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type.

7. Indices of refraction should be denoted by the symbols α, β, γ, ω, ε, n, and vibration directions by X, Y, Z, O and E.

Pergamon Press are also publishers of the following Journals:

JOURNAL OF NUCLEAR ENERGY (*including* THE SOVIET JOURNAL OF ATOMIC ENERGY*). PART A: REACTOR SCIENCE; PART B: REACTOR TECHNOLOGY; PART C: PLASMA PHYSICS—ACCELERATORS—THERMONUCLEAR REACTORS
HEALTH PHYSICS (*The Official Journal of the Health Physics Society*)
JOURNAL OF INORGANIC AND NUCLEAR CHEMISTRY
TETRAHEDRON (*The International Journal of Organic Chemistry*)
TALANTA (*An International Journal of Analytical Chemistry*)
INTERNATIONAL JOURNAL OF APPLIED RADIATION AND ISOTOPES
BIOCHEMICAL PHARMACOLOGY
ARCHIVES OF ORAL BIOLOGY
* BIOPHYSICS
* JOURNAL OF MICROBIOLOGY, EPIDEMOLOGY AND IMMUNOBIOLOGY
* PROBLEMS OF HEMATOLOGY AND BLOOD TRANSFUSION
* PROBLEMS OF VIROLOGY
* PROBLEMS OF ONCOLOGY
* SECHENOV PHYSIOLOGICAL JOURNAL OF THE U.S.S.R.
* PAVLOV JOURNAL OF HIGHER NERVOUS ACTIVITY
* ELECTRIC TECHNOLOGY, U.S.S.R.
* RADIO ENGINEERING
* RADIO ENGINEERING AND ELECTRONICS
* TELECOMMUNICATIONS
* PHYSICS OF METALS AND METALLOGRAPHY
* THE ABSTRACTS JOURNAL OF METALLURGY
* APPLIED MATHEMATICS AND MECHANICS
CHEMICAL ENGINEERING SCIENCE
JOURNAL OF ATMOSPHERIC AND TERRESTRIAL PHYSICS
PLANETARY AND SPACE SCIENCE
ANNALS OF THE INTERNATIONAL GEOPHYSICAL YEAR
SPECTROCHIMICA ACTA
JOURNAL OF THE MECHANICS AND PHYSICS OF SOLIDS
ACTA METALLURGICA (*for the Board of Governors of Acta Metallurgica*)
INTERNATIONAL JOURNAL OF THE PHYSICS AND CHEMISTRY OF SOLIDS
DEEP-SEA RESEARCH
JOURNAL OF NEUROCHEMISTRY
JOURNAL OF PSYCHOSOMATIC RESEARCH
JOURNAL OF INSECT PHYSIOLOGY
INTERNATIONAL JOURNAL OF AIR POLLUTION
INTERNATIONAL ABSTRACTS OF BIOLOGICAL SCIENCES (*for Biological and Medical Abstracts Ltd.*)
RHEOLOGY ABSTRACTS
VACUUM
OPERATIONAL RESEARCH QUARTERLY
ANNALS OF OCCUPATIONAL HYGIENE
ELECTROCHIMICA ACTA
JOURNAL OF CHILD PYSCHOLOGY AND PSYCHIATRY
JOURNAL OF SMALL ANIMAL PRACTICE
SOLID-STATE ELECTRONICS
INTERNATIONAL JOURNAL OF MECHANICAL SCIENCES

* *Translations of Russian journals published on behalf of the Pergamon Institute, a division of Pergamon International Corporation*

Leaflets giving further details and subscription rates of each of these journals are available on request

Jan19'61R

FILED IN STACKS

'65

THE GEOCHEMICAL SOCIETY

OFFICERS

Tom F. W. Barth, President
Harold C. Urey, Vice-President
Konrad B. Krauskopf, Secretary
George T. Faust, Treasurer

COUNCILLORS

E. F. Osborn, 1958–1960
H. G. Thode, 1958–1960
Albert E. J. Engel, 1959–1961
Friedrich G. Houtermans, 1959–1961
Ralph Cannon, 1960–1962
Th. G. Sahama, 1960–1962

REGIONAL VICE-PRESIDENTS

Louis H. Ahrens
Rui Ribeiro Franco
Ing. Georges Ordoñez
C. W. Correns
J. F. Lovering
Ken Sugawara

COMMITTEES

Auditing Committee:
Joseph J. Tregoning, Chairman
William L. Hill
C. R. Nasser

Constitution and By-Laws Committee:
Michael Fleischer, Chairman
Julian R. Goldsmith
Denis M. Shaw

Education Committee:
H. D. Holland, Chairman
J. A. S. Adams
D. M. Henderson
Kurt E. Lowe
G. D. Nicholls
Hans P. Eugster

Membership Committee:
R. M. Garrels, Chairman
Harvey C. Diebl
Chester B. Slawson
James E. Slosson
Irving Breger

Nominating Committee:
Wm. T. Pecora, Chairman
T. G. Sahama
C. E. Tilley
G. Tunell

Programme Committee:
H. T. Evans, Chairman
Gordon J. F. MacDonald
H. E. Lowenstam

Publications Committee:
E. W. Heinrich, Chairman
Julian R. Goldsmith
John C. Maxwell
N. W. Rakestraw
S. C. Robinson
L. R. Wager
Earl Ingerson

Research Committee:
C. G. Dodd, Chairman
W. F. Bradley
R. A. Rowland
T. G. Thompson

Russian Translations Committee:
Earl Ingerson

Standards Committee:
Alvin Van Valkenberg, Chairman
Michael Fleischer
Loren Stieff
George Switzer
George Tilton

Tellers Committee:
Charles Meyer, Chairman
Henry R. Cornwall
Colin O. Hutton